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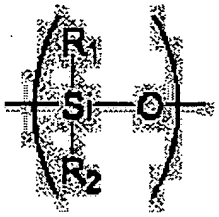
(54) ELECTROLYTE COMPOSITION, PHOTOELECTRIC CONVERSION ELEMENT AND PHOTOELECTRIC CELL

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an electrolyte composition having excellent durabilities and charge transporting ability as well as a photoelectric conversion element and a photoelectric cell using the composition that have excellent durabilities and photoelectric conversion properties.
SOLUTION: This electrolyte composition comprises a siloxane compound having a repeating unit represented by general formula (1) [R1 is L1-Q01 (L1 is a bond or a divalent bonding group; Q01 is a substituent group when L1 is a bond; and Q01 is a hydrogen atom or a substituent group when L1 is a divalent bonding group); and R2 is L2-Q02 (L2 is a bond or a divalent bonding group; Q02 is a substituent group when L2 is a bond; and Q02 is a hydrogen atom or a substituent group when L2 is a divalent bonding group)], and having at least two substituent groups that can form a covalent bond when reacted with an electrophilic agent. The composition may comprise a polymer obtained by reacting the siloxane compound with an electrophilic agent having at least two leaving groups. The composition is used for forming a photoconversion element and a photoelectric cell.



(1)

R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

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(54)【発明の名称】電解質組成物、光電変換素子及び光電池
(51)【国際特許分類第7版】

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【FI】

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4J035 BA01 CA042 CA181 GA05 LB20
5F051 AA14 BA18 EA18 FA01 FA02 KA10
5G301 CA30 CD01
5H032 AA06 AS16 CC17 EE04 HH01 HH02

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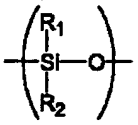
(57)【要約】
【課題】耐久性及び電荷輸送能に優れた電解質組成物、並びにこの電解質組成物を用いたために優れた耐久性及び光電変換特性を示す光電変換素子及び光電池を提供する。
【課題手段】下記一般式(1):【化1】

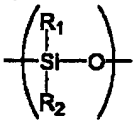


・・・(1)

R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

(ただし、R_1はL_1-Q_{01}(L_1は結合又は2価連結基を表し、L_1が結合を表すときQ_{01}は置換基を表し、L_1が2価連結基を表すときQ_{01}は水素原子又は置換基を表す。)を表し、R_2はL_2-Q_{02}(L_2は結合又は2価連結基を表し、L_2が結合を表すときQ_{02}は置換基を表し、L_2が2価連結基を表すときQ_{02}は水素原子又は置換基を表す。)を表す。)により表される繰り返し単位を含み、求電子剤と反応して共有結合を形成しうる置換基を少なくとも2つ有するシロキサン化合物を含有する電解質組成物、並びにこのシロキサン化合物と少なくとも2個の脱離基を有する求電子剤とを反応させて得られる重合体を含有する電解質組成物。また本発明の光電変換素子及び光電池は該電解質組成物を含む。

【特許請求の範囲】
【請求項1】下記一般式(1):【化1】



・・・(1)

R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

(ただし、R_1はL_1-Q_{01}(L_1は結合又は2価連結基を表し、L_1が結合を表すときQ_{01}は置換基を表し、L_1が2価連結基を表すときQ_{01}は水素原子又は置換基を表す。)を表し、R_2はL_2-Q_{02}(L_2は結合又は2

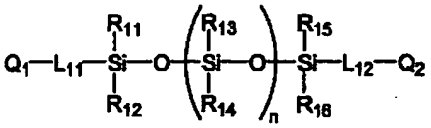
価連結基を表し、L_2が結合を表すときQ_{02}は置換基を表し、L_2が2価連結基を表すときQ_{02}は水素原子又は置換基を表す。)を表す。)により表される繰り返し単位を含み、求電子剤と反応して共有結合を形成しうる置換基を少なくとも2つ有するシロキサン化合物を含有することを特徴とする電解質組成物。

【請求項2】請求項1に記載の電解質組成物において、前記求電子剤と反応して共有結合を形成しうる置換基が塩基性基であることを特徴とする電解質組成物。

【請求項3】請求項2に記載の電解質組成物において、前記塩基性基に水素を付加してなる化合物の共役酸のpKaが3～15であることを特徴とする電解質組成物。

【請求項4】請求項2又は3に記載の電解質組成物において、前記塩基性基が置換若しくは無置換のピリジル基又は置換若しくは無置換のイミダゾリル基であることを特徴とする電解質組成物。

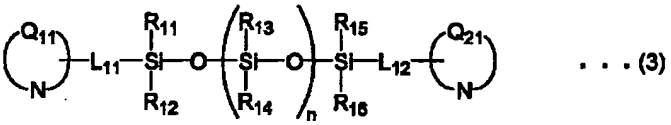
【請求項5】請求項1～4のいずれかに記載の電解質組成物において、前記シロキサン化合物が下記一般式(2):【化2】



・・・(2)

(ただし、Q_1及びQ_2はそれぞれ独立に前記求電子剤と反応して共有結合を形成しうる置換基を表し、R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基又は置換若しくは無置換のアリール基を表し、L_{11}及びL_{12}はそれぞれ独立に2価連結基を表し、nは1～1000の整数を表す。)により表されることを特徴とする電解質組成物。

【請求項6】請求項5に記載の電解質組成物において、前記シロキサン化合物が下記一般式(3):【化3】



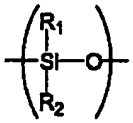
・・・(3)

(ただし、Q_{11}及びQ_{21}はそれぞれ独立に窒素原子と共に5又は6員環を形成する原子団を表し、R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基又は置換若しくは無置換のアリール基を表し、L_{11}及びL_{12}はそれぞれ独立に2価連結基を表し、nは1～1000の整数を表す。)により表されることを特徴とする電解質組成物。

【請求項7】請求項6に記載の電解質組成物において、前記Q_{11}及びQ_{21}がそれぞれ炭素原子、水素原子、窒素原子、酸素原子及び硫黄原子からなる群から選ばれる1種以上の原子により構成されることを特徴とする電解質組成物。

【請求項8】請求項6又は7に記載の電解質組成物において、前記5又は6員環がイミダゾール環又はピリジン環であることを特徴とする電解質組成物。

【請求項9】少なくとも2個の脱離基を有する求電子剤と、下記一般式(1):【化4】



・・・(1)

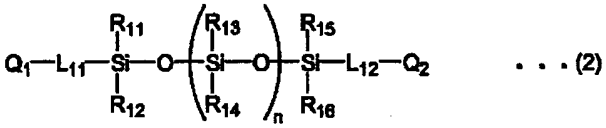
R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

(ただし、R_1はL_1-Q_{01}(L_1は結合又は2価連結基を表し、L_1が結合を表すときQ_{01}は置換基を表し、L_1が2価連結基を表すときQ_{01}は水素原子又は置換基を表す。)を表し、R_2はL_2-Q_{02}(L_2は結合又は2価連結基を表し、L_2が結合を表すときQ_{02}は置換基を表し、L_2が2価連結基を表すときQ_{02}は水素原

子又は置換基を表す。)を表す。)により表される繰り返し単位を含み、前記求電子剤と反応して共有結合を形成しうる置換基を少なくとも2つ有するシロキサン化合物とを反応させて得られる重合体を含有することを特徴とする電解質組成物。

【請求項10】請求項9に記載の電解質組成物において、前記シロキサン化合物が下記一般式(2):

【化5】

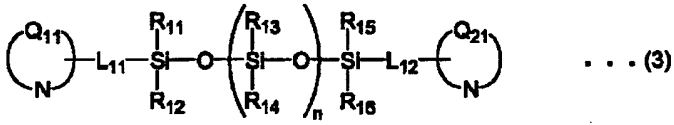


・・・(2)

(ただし、Q_1及びQ_2はそれぞれ独立に前記求電子剤と反応して共有結合を形成しうる置換基を表し、R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基又は置換若しくは無置換のアリール基を表し、L_{11}及びL_{12}はそれぞれ独立に2価連結基を表し、nは1～1000の整数を表す。)により表されることを特徴とする電解質組成物。

【請求項11】請求項10に記載の電解質組成物において、前記シロキサン化合物が下記一般式(3):

【化6】



・・・(3)

(ただし、Q_{11}及びQ_{21}はそれぞれ独立に窒素原子と共に5又は6員環を形成する原子団を表し、R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基又は置換若しくは無置換のアリール基を表し、L_{11}及びL_{12}はそれぞれ独立に2価連結基を表し、nは1～1000の整数を表す。)により表されることを特徴とする電解質組成物。

【請求項12】請求項9～11のいずれかに記載の電解質組成物において、前記脱離基が脱離して生じるアニオンの共役酸のpKaが10以下であることを特徴とする電解質組成物。

【請求項13】請求項9～12のいずれかに記載の電解質組成物において、前記脱離基がそれぞれハロゲン原子、アルキルスルホニルオキシ基又はアリールスルホニルオキシ基であることを特徴とする電解質組成物。

【請求項14】請求項1～13のいずれかに記載の電解質組成物において、溶媒含有量が電解質組成物全体の10質量%以下であることを特徴とする電解質組成物。

【請求項15】請求項1～14のいずれかに記載の電解質組成物において、前記シロキサン化合物及び前記重合体以外にヨウ素塩及び／又はヨウ素を含有することを特徴とする電解質組成物。

【請求項16】請求項1～15のいずれかに記載の電解質組成物において、光電池に用いられることを特徴とする電解質組成物。

【請求項17】導電層、感光層、電荷輸送層及び対極を有する光電変換素子において、前記電荷輸送層が請求項1～16のいずれかに記載の電解質組成物を含有することを特徴とする光電変換素子。

【請求項18】請求項17に記載の光電変換素子において、前記感光層が色素によって増感された半導体微粒子を含有することを特徴とする光電変換素子。

【請求項19】請求項18に記載の光電変換素子において、前記半導体微粒子が金属カルコゲニド微粒子を含むことを特徴とする光電変換素子。

【請求項20】請求項19に記載の光電変換素子において、前記金属カルコゲニド微粒子が酸化チタン微粒子を含むことを特徴とする光電変換素子。

【請求項21】請求項17～20のいずれかに記載の光電変換素子において、前記色素が金属錯体色素及び／又はポリメチン色素であることを特徴とする光電変換素子。

【請求項22】請求項17～21のいずれかに記載の光電変換素子を用いた光電池。

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(51)Int.Cl.'	識別記号	F I		テーマコード'(参考)
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77/26			77/26	4J035
C08K 3/02		C08K 3/02		5F051
C08L 83/04		C08L 83/04		5G301
H01B 1/06		H01B 1/06	A	5H032

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(33)優先権主張国　日本（J P）

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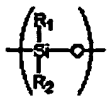
(54)【発明の名称】　電解質組成物、光電変換素子及び光電池

(57)【要約】
【課題】　耐久性及び電荷輸送能に優れた電解質組成物．並びにこの電解質組成物を用いたために優れた耐久性及び光電変換特性を示す光電変換素子及び光電池を提供する。
【課題手段】　下記一般式(1)：
【化1】



・・・(1)

R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

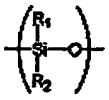
（ただし、R_1はL_1-Q_{01}（L_1は結合又は2価連結基を表し．L_1が結合を表すときQ_{01}は置換基を表し．L_1が2価連結基を表すときQ_{01}は水素原子又は置換基を表す。）を表し、R_2はL_2-Q_{02}（L_2は結合又は2価連結基を表し、L_2が結合を表すときQ_{02}は置換基を表し、L_2が2価連結基を表すときQ_{02}は水素原子又は置換基を表す。）を表す。）により表される繰り返し単位を含み、求電子剤と反応して共有結合を形成しうる置換基を少なくとも2つ有するシロキサン化合物を含有する電解質組成物．並びにこのシロキサン化合物と少なくとも2個の脱離基を有する求電子剤とを反応させて得られる重合体を含有する電解質組成物。また本発明の光電変換素子及び光電池は該電解質組成物を含む。

1

【特許請求の範囲】

【請求項１】 下記一般式(1)：

【化１】



・・・(1)

R_1: L_1-Q_{01}

R_2: L_2-Q_{02}

（ただし、R_1はL_1-Q_{01}（L_1は結合又は２価連結基を表し、L_1が結合を表すときQ_{01}は置換基を表し、L_1が２価連結基を表すときQ_{01}は水素原子又は置換基を表す。）を表し、R_2はL_2-Q_{02}（L_2は結合又は２価連結基を表し、L_2が結合を表すときQ_{02}は置換基を表し、L_2が２価連結基を表すときQ_{02}は水素原子又は置換基を表す。）を表す。）により表される繰り返し単位を含み、求電子剤と反応して共有結合を形成しうる置換基を少なくとも２つ有するシロキサン化合物を含有することを特徴とする電解質組成物。

【請求項２】 請求項１に記載の電解質組成物において．前記求電子剤と反応して共有結合を形成しうる置換基が塩基性基であることを特徴とする電解質組成物。

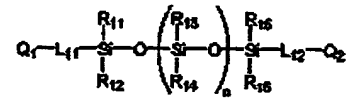
【請求項３】 請求項２に記載の電解質組成物において．前記塩基性基に水素を付加してなる化合物の共役酸＊のpKaが３～15であることを特徴とする電解質組成物。

2

【請求項４】 請求項２又は３に記載の電解質組成物において、前記塩基性基が置換若しくは無置換のピリジル基又は置換若しくは無置換のイミダゾリル基であることを特徴とする電解質組成物。

【請求項５】 請求項１～４のいずれかに記載の電解質組成物において．前記シロキサン化合物が下記一般式(2)：

【化２】

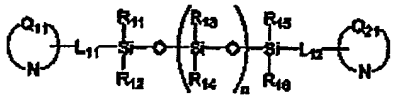


・・・(2)

（ただし、Q_1及びQ_2はそれぞれ独立に前記求電子剤と反応して共有結合を形成しうる置換基を表し、R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基又は置換若しくは無置換のアリール基を表し．L_{11}及びL_{12}はそれぞれ独立に２価連結基を表し、nは１～1000の整数を表す。）により表されることを特徴とする電解質組成物。

【請求項６】 請求項５に記載の電解質組成物において．前記シロキサン化合物が下記一般式(3)：

【化３】



・・・(3)

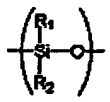
（ただし、Q_{11}及びQ_{21}はそれぞれ独立に窒素原子と共に５又は６員環を形成する原子団を表し．R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基又は置換若しくは無置換のアリール基を表し、L_{11}及びL_{12}はそれぞれ独立に２価連結基を表し．nは１～1000の整数を表す。）により表されることを特徴とする電解質組成物。

【請求項７】 請求項６に記載の電解質組成物において．前記Q_{11}及びQ_{21}がそれぞれ炭素原子、水素原子、窒素原子、酸素原子及び硫黄原子からなる群から選ばれる１種以上の原子により構成されることを特徴とする電解質組成物。

【請求項８】 請求項６又は７に記載の電解質組成物において、前記５又は６員環がイミダゾール環又はピリジン環であることを特徴とする電解質組成物。

【請求項９】 少なくとも２個の脱離基を有する求電子剤と．下記一般式(1)：

【化４】



・・・(1)

R_1: L_1-Q_{01}

R_2: L_2-Q_{02}

（ただし、R_1はL_1-Q_{01}（L_1は結合又は２価連結基を表し．L_1が結合を表すときQ_{01}は置換基を表し．L_1が２価連結基を表すときQ_{01}は水素原子又は置換基を表す。）を表し、R_2はL_2-Q_{02}（L_2は結合又は２価連結基を表し、L_2が結合を表すときQ_{02}は置換基を表し、L_2が２価連結基を表すときQ_{02}は水素原子又は置換基を表す。）を表す。）により表される繰り返し単位を含み、前記求電子剤と反応して共有結合を形成しうる置換基を少なくとも２つ有するシロキサン化合物とを反応させて得られる錯体を含有することを特徴とする電解質組成物。

【請求項10】 請求項９に記載の電解質組成物において．前記シロキサン化合物が下記一般式(2)：

【化５】

3

・・・(2)

（ただし、Q_1及びQ_2はそれぞれ独立に前記求電子剤と反応して共有結合を形成しうる置換基を表し、R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基又は置換若しくは無置換のアリール基を表し、L_{11}及びL_{12}はそれぞれ独立に２価連結基を表し、nは１～1000の整数を表す。）により表されることを特徴とする電解質組成物。

【請求項12】 請求項９～11のいずれかに記載の電解質組成物において、前記脱離基が脱離して生じるアニオンの共役酸のpKaが10以下であることを特徴とする電解質組成物。

【請求項13】 請求項９～12のいずれかに記載の電解質組成物において、前記脱離基がそれぞれハロゲン原子、アルキルスルホニルオキシ基又はアリールスルホニルオキシ基であることを特徴とする電解質組成物。

【請求項14】 請求項１～13のいずれかに記載の電解質組成物において、溶媒含有量が電解質組成物全体の10質量%以下であることを特徴とする電解質組成物。

【請求項15】 請求項１～14のいずれかに記載の電解質組成物において、前記シロキサン化合物及び前記重合体以外にヨウ素塩及び／又はヨウ素を含有することを特徴とする電解質組成物。

【請求項16】 請求項１～15のいずれかに記載の電解質組成物において、光電池に用いられることを特徴とする電解質組成物。

【請求項17】 導電層、感光層、電荷輸送層及び対極を有する光電変換素子において、前記電荷輸送層が請求項１～16のいずれかに記載の電解質組成物を含有することを特徴とする光電変換素子。

【請求項18】 請求項17に記載の光電変換素子において、前記感光層が色素によって増感された半導体微粒子を含有することを特徴とする光電変換素子。

【請求項19】 請求項18に記載の光電変換素子において、前記半導体微粒子が金属カルコゲニド微粒子を含むことを特徴とする光電変換素子。

【請求項20】 請求項19に記載の光電変換素子において、前記金属カルコゲニド微粒子が酸化チタン微粒子を含むことを特徴とする光電変換素子。

【請求項21】 請求項17～20のいずれかに記載の光電変換素子において、前記色素が金属錯体色素及び／又はポリメチン色素であることを特徴とする光電変換素子。

【請求項22】 請求項17～21のいずれかに記載の光電変換素子を用いた光電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、耐久性及び電荷輸送能に優れた電解質組成物、並びにこの電解質組成物を用いたために優れた耐久性及び光電変換特性を示す光電変換素子及び光電池に関する。

【０００２】

【従来の技術】従来から電池、キャパシター、センサー、表示素子、記録素子等の電気化学的素子の電解質として、溶媒に電解質塩を溶解した液状電解質組成物（電解液）が用いられてきた。しかしながら、このような液状電解質組成物を用いた電気化学的素子においては、長期間の使用又は保存の間に該組成物が漏洩することがあり、信頼性に欠ける。

【０００３】Nature, 第353巻, 第737～740頁, 1991年, 米国特許4927721号等は色素により増感した半導体微粒子を用いた光電変換素子及びこれを用いた光電気化学電池を開示しているが、これらにおいても電荷輸送層に液状電解質組成物を用いているため、長期間の使用又は保存の間に該組成物が漏洩又は枯渇し、光電変換効率が著しく低下したり、素子として機能しなくなる場合がある。

【０００４】このような状況下、WO 93/20565号は固体電解質を用いた光電変換素子を提案した。また日本化学会誌, 7, 484頁 (1997)、特開平7-288142号, Solid State Ionics, 89, 263 (1986)及び特開平9-27352号は、架橋ポリエチレンオキサイド系高分子化合物を用いた固体電解質を含む光電変換素子を提案した。しかしながら、これらの固体電解質を用いた光電変換素子は光電変換特性、特に短絡電流密度が不十分であり、加えて耐久性も十分ではない。

【０００５】また、電解質組成物の漏洩及び枯渇を防止し光電変換素子の耐久性を向上させるために、ピリジニウム塩、イミダゾリウム塩、トリアゾリウム塩等を用いる方法が開示されている（WO 95/18456号, 特開平8-259543号, 電気化学, 第65巻, 11号, 923頁 (1997年)

剤が有する脱離基が脱離して生じるアニオンの共役酸のpKaは10以下であるのが好ましい。

【００１７】(6)第二の電解質組成物において、求電子剤が有する脱離基はそれぞれハロゲン原子、アルキルスルホニルオキシ基又はアリールスルホニルオキシ基であるのが好ましい。

【００１８】(7)第一及び第二の電解質組成物の溶媒含有量は電解質組成物全体の10質量%以下であるのが特に好ましい。

【００１９】(8)第一及び第二の電解質組成物は上記シロキサン化合物及び上記重合体以外にヨウ素塩及び／又はヨウ素を含有するのが好ましい。

【００２０】(9)光電変換素子の感光層は色素によって増感された半導体微粒子を含有するのが好ましい。この半導体微粒子は金属カルコゲナイド微粒子を含むのが好ましく、金属カルコゲナイド微粒子は酸化チタン微粒子を含むのが好ましい。また、色素は金属錯体色素及び／又はポリメチン色素であるのが好ましい。

【００２１】

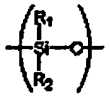
【発明の実施の形態】[1]電解質組成物

本発明の第一の電解質組成物は後述する特定のシロキサン化合物を含有する。また、本発明の第二の電解質組成物はこのシロキサン化合物を少なくとも２個の脱離基を有する求電子剤と反応させて得られる重合体を含有する。本発明の第二の電解質組成物は流動性を殆ど示さず、耐久性及び電荷輸送能に優れている。本発明の第一及び第二の電解質組成物は更に電解質塩、溶媒等を含有してもよい。以下、本発明の第一及び第二の電解質組成物の各構成要素について詳述する。

【００２２】(A)シロキサン化合物

本発明の第一及び第二の電解質組成物に用いるシロキサン化合物は、下記一般式(1)により表される繰り返し単位を含み、且つ求電子剤と反応して共有結合を形成しうる置換基を少なくとも２つ有する。本発明の第二の電解質組成物においては、このシロキサン化合物は求電子剤によりアルキル化、４級化等の修飾を受ける。

【化10】



・・・(1)

R_1: L_1-Q_{01}

R_2: L_2-Q_{02}

【００２３】一般式(1)中、R_1はL_1-Q_{01}を表し、R_2はL_2-Q_{02}を表す。ここで、L_1は結合又は２価連結基を表し、L_1が結合を表すときQ_{01}は置換基を表し、L_1が２価連結基を表すときQ_{01}は水素原子又は置換基を表す。また、L_2は結合又は２価連結基を表し、L_2が結合を表すときQ_{02}は置換基を表し、L_2が２価連結基を表すときQ_{02}は水素原子又は置換基を表す。シロキサン化合物は一般式(1)

により表される繰り返し単位を１つ含んでも複数含んでもよく、複数含む場合は各繰り返し単位中のR_1及びR_2はそれぞれ同じでも異なっていてもよい。

【００２４】L_1又はL_2が２価連結基を表す場合、その例としてはアルキレン基、アルケニレン基、アリーレン基、-O-、-S-、-CO-、-NR'-（R'は水素原子又はアルキル基）、$-SO_2-$、-SiR''R'''-（R''及びR'''はそれぞれアルキル基、アリール基、アルコキシ基又はアリールオキシ基）、これらの組み合わせ等が挙げられ、中でも-$(CH_2)_{n1}$-、-O-、-$(OCH_2CH_2)_{n1}$-、-$(OCH_2CH_2)_{n1}$-O-、-$(OCH_2CH_2)_{n1}$-CH_2-、-$(OCH_2CH_2CH_2)_{n1}$-、-$(OCH_2CH_2CH_2)_{n1}$-O-、-$(OCH_2CH_2CH_2)_{n1}$-CH_2-、-$(CH_2)_{n1}$-$(Si(CH_3)_2-O)_{n2}$-及び-O-$(CH_2)_{n1}$-$(Si(CH_3)_2-O)_{n2}$-が好ましい。なおn1、n2はそれぞれ１～20の整数を表す。

【００２５】Q_{01}及びQ_{02}が置換基を表す場合、好ましい置換基の例としてはアルキル基（直鎖状、分岐状又は環状であってよく、例えばメチル基、エチル基、n-プロピル基、イソプロピル基、t-ブチル基、n-オクチル基、エイコシル基、2-クロロエチル基、2-シアノエチル基、2-エチルヘキシル基、シクロヘキシル基、シクロペンチル基、4-n-ドデシルシクロヘキシル基等）、アリール基（例えばフェニル基、p-トリル基、ナフチル基、m-クロロフェニル基等）、ヘテロ環基（好ましくは５又は６員の置換又は無置換の芳香族ヘテロ環化合物又は非芳香族ヘテロ環化合物から１個の水素原子を取り除いてなる１価の基であり、例えば2-フリル基、2-チエニル基、2-ピリミジニル基、2-ピリジル基、4-ピリジル基、1-イミダゾリル基等）、ハロゲン原子（例えば塩素原子、臭素原子、ヨウ素原子等）、シアノ基、ニトロ基、水酸基、アルコキシ基（例えばメトキシ基、エトキシ基、イソプロポキシ基、t-ブトキシ基、n-オクチルオキシ基、2-メトキシエトキシ基、-$O(CH_2CH_2O)_6CH_3$等）、シリルオキシ基（例えばトリメチルシリルオキシ基、t-ブチルジメチルシリルオキシ基、トリメトキシシリルオキシ基等）、アシルオキシ基（例えばホルミルオキシ基、アセチルオキシ基、ピバロイルオキシ基、ステアロイルオキシ基、ベンゾイルオキシ基、p-メトキシフェニルカルボニルオキシ基等）、カルバモイルオキシ基（例えばN,N-ジメチルカルバモイルオキシ基、N,N-ジエチルカルバモイルオキシ基、モルホリノカルボニルオキシ基、N,N-ジ-n-オクチルアミノカルボニルオキシ基、N-n-オクチルカルバモイルオキシ基等）、アルコキシカルボニルオキシ基（例えばメトキシカルボニルオキシ基、エトキシカルボニルオキシ基、t-ブトキシカルボニルオキシ基、n-オクチルカルボニルオキシ基等）、アリールオキシカルボニルオキシ基（例えばフェノキシカルボニルオキシ基、p-メトキシフェノキシカルボニルオキシ基、p-n-ヘキサデシルオキシフェノキシカルボニルオキシ基等）、アミノ基（例えばアミノ基、メチルアミノ基、ジメチルアミノ基、アニリノ基、N-メチルアニリノ基、ジフェニルアミ

等）。これらの塩は常温（25℃付近）において溶融状態にあり、室温溶融塩と呼ばれる。この方法では水や有機溶媒等の溶媒が不要或いは少量で済むため、電池の耐久性が向上する。しかしながら、これらの室温溶融塩を用いた光電変換素子は特に開放電圧が低く、光電変換効率が良くない。

【０００６】

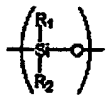
【発明が解決しようとする課題】従って本発明の目的は、耐久性及び電荷輸送能に優れた電解質組成物、並びにこの電解質組成物を用いたために優れた耐久性及び光電変換特性を示す光電変換素子及び光電池を提供することである。

【０００７】

【課題を解決するための手段】上記目的に鑑み鋭意研究の結果、本発明者は、特定の繰り返し単位を含むシロキサン化合物を含有する電解質組成物、並びに該シロキサン化合物を求電子剤と反応させて得られる重合体を含有する電解質組成物は優れた電荷輸送能及び耐久性を示すことを発見し、本発明に想到した。

【０００８】即ち、本発明の第一の電解質組成物は下記一般式(1)：

【化７】



・・・(1)

R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

（ただし、R_1はL_1-Q_{01}（L_1は結合又は２価連結基を表し、L_1が結合を表すときQ_{01}は置換基を表し、L_1が２価連結基を表すときQ_{01}は水素原子又は置換基を表す。）を表し、R_2はL_2-Q_{02}（L_2は結合又は２価連結基を表し、L_2が結合を表すときQ_{02}は置換基を表し、L_2が２価連結基を表すときQ_{02}は水素原子又は置換基を表す。）を表す。）により表される繰り返し単位を含み、求電子剤と反応して共有結合を形成しうる置換基を少なくとも２つ有するシロキサン化合物を含有することを特徴とする。

【０００９】また、本発明の第二の電解質組成物は少なくとも２個の脱離基を有する求電子剤と、上記一般式(1)により表される繰り返し単位を含み、求電子剤と反応して共有結合を形成しうる置換基を少なくとも２つ有するシロキサン化合物とを反応させて得られる重合体を含有することを特徴とする。

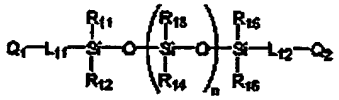
【００１０】本発明の第一及び第二の電解質組成物は光電池に好ましく用いることができる。本発明の光電変換素子は導電層、感光層、電荷輸送層及び対極を有し、該電荷輸送層が上記第一の電解質組成物又は第二の電解質組成物を含有することを特徴とする。本発明の光電池はこの光電変換素子を用いたものである。

【００１１】本発明では下記条件を満たすことにより、一層優れた耐久性又は電荷輸送能を有する電解質組成物、並びに一層優れた耐久性及び光電変換特性を示す光電変換素子及び光電池が得られる。

【００１２】(1)第一及び第二の電解質組成物において、求電子剤と反応して共有結合を形成しうる置換基は塩基性基であるのが好ましく、この塩基性基は特に好ましくは置換若しくは無置換のピリジル基又は置換若しくは無置換のイミダゾリル基である。該塩基性基に水素を付加してなる化合物の共役酸のpKaは３～15であるのが好ましい。

【００１３】(2)第一及び第二の電解質組成物に用いるシロキサン化合物は下記一般式(2)により表されるのが好ましく、下記一般式(3)により表されるのがより好ましい。

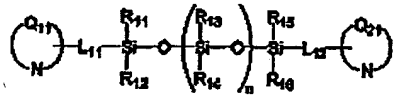
【化８】



・・・(2)

一般式(2)中、Q_1及びQ_2はそれぞれ独立に上記求電子剤と反応して共有結合を形成しうる置換基を表し、R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基又は置換若しくは無置換のアリール基を表し、L_{11}及びL_{12}はそれぞれ独立に２価連結基を表し、nは１～1000の整数を表す。

【化９】



・・・(3)

一般式(3)中、Q_{11}及びQ_{21}はそれぞれ独立に窒素原子と共に５又は６員環を形成する原子団を表し、R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基又は置換若しくは無置換のアリール基を表し、L_{11}及びL_{12}はそれぞれ独立に２価連結基を表し、nは１～1000の整数を表す。

【００１４】(3)第一及び第二の電解質組成物において、一般式(3)中のQ_{11}及びQ_{21}はそれぞれ炭素原子、水素原子、窒素原子、酸素原子及び硫黄原子からなる群から選ばれる１種以上の原子により構成されるのが好ましい。

【００１５】(4)第一及び第二の電解質組成物において、一般式(3)中のQ_{11}及びQ_{21}がそれぞれ窒素原子と共に形成する５又は６員環はイミダゾール環又はピリジン環であるのが特に好ましい。

【００１６】(5)第二の電解質組成物において、求電子

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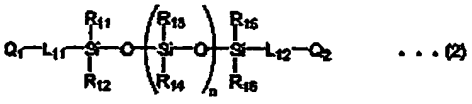
ノ基等）、アシルアミノ基（例えばホルミルアミノ基、アセチルアミノ基、ピバロイルアミノ基、ラウロイルアミノ基、ベンゾイルアミノ基、3,4,5-トリ-n-オクチルオキシフェニルカルボニルアミノ基等）、アミノカルボニルアミノ基（例えばカルバモイルアミノ基、N,N-ジメチルアミノカルボニルアミノ基、N,N-ジエチルアミノカルボニルアミノ基、モルホリノカルボニルアミノ基等）、アルコキシカルボニルアミノ基（例えばメトキシカルボニルアミノ基、エトキシカルボニルアミノ基、t-ブトキシカルボニルアミノ基、n-オクタデシルオキシカルボニルアミノ基、N-メチルメトキシカルボニルアミノ基等）、アリールオキシカルボニルアミノ基（例えばフェノキシカルボニルアミノ基、p-クロロフェノキシカルボニルアミノ基、m-n-オクチルオキシフェノキシカルボニルアミノ基等）、スルファモイルアミノ基（例えばスルファモイルアミノ基、N,N-ジメチルアミノスルホニルアミノ基、N-n-オクチルアミノスルホニルアミノ基等）、アルキルスルホニルアミノ基（例えばメチルスルホニルアミノ基、ブチルスルホニルアミノ基等）、アリールスルホニルアミノ基（例えばフェニルスルホニルアミノ基、2,3,5-トリクロロフェニルスルホニルアミノ基、p-メチルフェニルスルホニルアミノ基等）、メルカプト基、アルキルチオ基（例えばメチルチオ基、エチルチオ基、n-ヘキサデシルチオ基等）、アリールチオ基（例えばフェニルチオ基、p-クロロフェニルチオ基、m-メトキシフェニルチオ基等）、ヘテロ環チオ基（例えば2-ベンゾチアゾリルチオ基、1-フェニルテトラゾール-5-イルチオ基等）、スルファモイル基（例えばN-エチルスルファモイル基、N-(3-ドデシルオキシプロピル)スルファモイル基、N,N-ジメチルスルファモイル基、N-アセチルスルファモイル基、N-ベンゾイルスルファモイル基、N-(N'-フェニルカルバモイル)スルファモイル基等）、アルキルスルフィニル基（例えばメチルスルフィニル基、エチルスルフィニル基等）、アリールスルフィニル基（例えばフェニルスルフィニル基、p-メチルフェニルスルフィニル基等）、アルキルスルホニル基（例えばメチルスルホニル基、エチルスルホニル基等）、アリールスルホニル基（例えばフェニルスルホニル基、p-メチルフェニルスルホニル基等）、アシル基（例えばアセチル基、ピバロイル基、2-クロロアセチル基、ステアロイル基、ベンゾイル基、p-n-オクチルオキシフェニルカルボニル基等）、アリールオキシカルボニル基（例えばフェノキシカルボニル基、o-クロロフェノキシカルボニル基、m-ニトロフェノキシカルボニル基、p-t-ブチルフェノキシカルボニル基等）、アルコキシカルボニル基（例えばメトキシカルボニル基、エトキシカルボニル基、t-ブトキシカルボニル基、n-オクタデシルオキシカルボニル基等）、カルバモイル基（例えばカルバモイル

基、N-メチルカルバモイル基、N,N-ジメチルカルバモイル基、N,N-ジ-n-オクチルカルバモイル基、N-(メチルスルホニル)カルバモイル基等）、シリル基（好ましくは炭素数３～30の置換又は無置換のシリル基であり、例えばトリメチルシリル基、t-ブチルジメチルシリル基、フェニルジメチルシリル基等）、ホスフィノ基（好ましくは炭素数２～30の置換又は無置換のホスフィノ基であり、例えばジメチルホスフィノ基、ジフェニルホスフィノ基、メチルフェノキシホスフィノ基等）等が挙げられる。中でも、アルキル基、アリール基、シリル基、アルコキシ基、アリールオキシ基、シリルオキシ基、ヘテロ環基、アミノ基、アルキルチオ基及びホスフィノ基がより好ましく、アルキル基、シリル基、アルコキシ基、シリルオキシ基及びヘテロ環基が特に好ましい。

【００２６】上記シロキサン化合物は求電子剤と反応して共有結合を形成しうる置換基を２つ以上有する。第一及び第二の電解質組成物において、求電子剤と反応して共有結合を形成しうる置換基は塩基性基であるのが好ましい。ここで塩基性基とは、それに水素を付加してなる化合物の共役酸のpKaが３以上の基を指す。この共役酸のpKaは３～15であるのが好ましく、４～12であるのがより好ましい。このような塩基性基は、アミノ基（ジメチルアミノ基、ジエチルアミノ基、アニリノ基等）、含窒素複素環基（モルホリノ基、キヌクリジニル基、ピペラジニル基、ピペリジノ基、ピロリジノ基、イミダゾリル基、2-メチルイミダゾリル基、キノリル基、アクリジニル基、ピリジル基、2-メチルピリジル基、ジアザビシクロウンデセニル基等）又はグアニジノ基（トリメチルグアニジノ基等）であるのが好ましく、含窒素複素環基であるのがより好ましく、置換若しくは無置換のピリジル基又は置換若しくは無置換のイミダゾリル基であるのが特に好ましい。上記シロキサン化合物はこのような塩基性基を一般式(1)により表される繰り返し単位中の側鎖及び／又は末端に有してよい。この塩基性基を一般式(1)により表される繰り返し単位中の側鎖に有する場合、一般式(1)中のQ_{11}及び／又はQ_{12}が該塩基性基である。

【００２７】本発明の第一及び第二の電解質組成物に用いるシロキサン化合物は、下記一般式(2)により表されるのが好ましく、下記一般式(3)により表されるのがより好ましい。

【化11】



・・・(2)

【化12】

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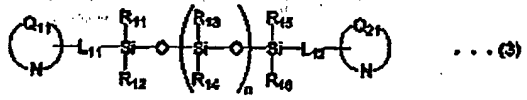
11　　12



...(3)

【００２８】一般式(2)中、Q_1及びQ_2はそれぞれ独立に求電子剤と反応して共有結合を形成しうる置換基を表す。この置換基中の求電子剤と反応する原子は好ましくは窒素原子、リン原子又は硫黄原子であり、より好ましくは窒素原子又はリン原子であり、特に好ましくは窒素原子である。Q_1及びQ_2が表す置換基としては、アミノ基、ホスフィノ基、複素環基、アルキルチオ基等が挙げられる。

【００２９】一般式(2)中、R_{11}～R_{16}はそれぞれ独立に置換若しくは無置換のアルキル基、又は置換若しくは無置換のアリール基を表す。R_{11}～R_{16}は好ましくは炭素数１～10のアルキル基であり、より好ましくは炭素数１～３のアルキル基であり、特に好ましくはメチル基である。

【００３０】上記Q_1、Q_2及びR_{11}～R_{16}はそれぞれ置換基を有していてもよい。該置換基の好ましい例としては、アルキル基（メチル基、エチル基、プロピル基、イソプロピル基、ブチル基、ペンチル基、ヘキシル基、オクチル基、2-エチルヘキシル基、t-オクチル基、デシル基、ドデシル基、テトラデシル基、2-ヘキシルデシル基、オクタデシル基、シクロヘキシル基、シクロペンチル基、2-カルボキシエチル基、ベンジル基等）、アルケニル基（ビニル基、アリル基等）、ハロゲン原子（フッ素原子、塩素原子、臭素原子、ヨウ素原子等）、シアノ基、アルコキシ基（メトキシ基、エトキシ基、メトキシエトキシ基等）、アリーロキシ基（フェノキシ基等）、アルキルチオ基（メチルチオ基、エチルチオ基等）、アシル基（アセチル基、プロピオニル基、ベンゾイル基等）、スルホニル基（メタンスルホニル基、ベンゼンスルホニル基等）、アシルオキシ基（アセトキシ基、ベンゾイルオキシ基等）、スルホニルオキシ基（メタンスルホニルオキシ基、トルエンスルホニルオキシ基等）、ホスホニル基（ジエチルホスホニル基等）、アミド基（アセチルアミノ基、ベンゾイルアミノ基等）、カルバモイル基（N,N-ジメチルカルバモイル基、N-フェニルカルバモイル基等）、アリール基（フェニル基、トルイル基等）、複素環基（ピリジル基、イミダゾリル基、フラニル基等）等が挙げられる。

【００３１】一般式(2)中、L_{11}及びL_{12}はそれぞれ独立に２価連結基を表す。この２価連結基の例としては、アルキレン基、アルケニレン基、アリーレン基、-O-、-S-、-CO-、-NR'-（R'は水素原子又はアルキル基を表す）、$-SO_2-$、-SiRR'-（R及びR'はそれぞれアルキル基又はアリール基を表す）、これらを２つ以上組み合わせてなる連結基等が挙げられる。

【００３２】L_{11}及びL_{12}がアルキレン基、アルケニレン基又はアリーレン基である場合、これらはハロゲン原子（フッ素原子、塩素原子、臭素原子、ヨウ素原子等）、水酸基、アミノ基、ニトロ基、カルボキシル基、カルバモイル基、スルホン酸基、スルホンアミド基、アシル基（ホルミル基、アセチル基等）、アシルオキシ基、アシルアミノ基（アセトアミノ基、ベンズアミノ基等）、アルキル基、アルコキシ基（メトキシ基、エトキシ基、メトキシエトキシ基等）、アコキシカルボニル基、アルキルスルホニル基、アリール基、アリールオキシ基（フェノキシ基等）、アリールスルホニル基等の置換基を有していてもよい。

【００３３】一般式(2)中、nは１～1000の整数を表す。nは好ましくは１～500の整数であり、特に好ましくは１～100の整数である。nが1000よりも大きいと、イオン伝導度及び求電子剤との反応性の低下を招く。

【００３４】一般式(3)中、Q_{21}及びQ_{22}はそれぞれ独立に窒素原子と共に５又は６員環を形成する原子団を表す。Q_{21}及びQ_{22}は炭素原子、水素原子、窒素原子、酸素原子及び硫黄原子からなる群から選ばれる１種以上の原子により構成されるのが好ましい。

【００３５】Q_{21}及びQ_{22}により形成される５又は６員環は不飽和環であるのが好ましい。５員環としてはピロリジン環、オキサゾール環、チアゾール環、イミダゾール環、ピラゾール環、イソオキサゾール環、チアジアゾール環、オキサジアゾール環及びトリアゾール環が好ましく、チアゾール環、イミダゾール環及びトリアゾール環がより好ましく、イミダゾール環が特に好ましい。６員環としてはモルホリン環、ピペリジン環、ピリジン環、ピリミジン環、ピリダジン環、ピラジン環及びトリアジン環が好ましく、ピリジン環が特に好ましい。

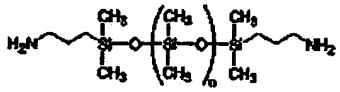
【００３６】一般式(3)中のR_{31}～R_{36}、L_{31}及びL_{32}、並びにnは一般式(2)中のそれらと同義であり、好ましい態様も同様である。

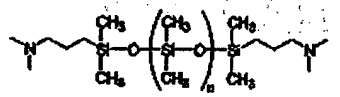
【００３７】本発明の第一及び第二の電解質組成物に用いるシロキサン化合物の具体例1-1～1-18を以下に示すが、本発明はそれらに限定されるものではない。

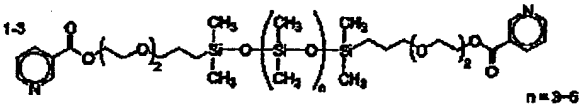
【００３８】

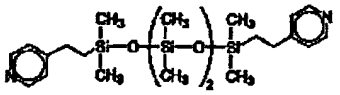
【化13】

13 14

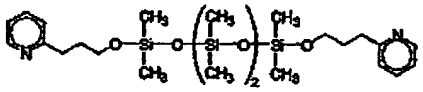
1-1  n＝8-10

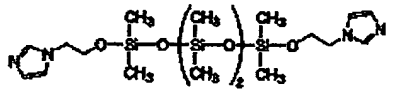
1-2  n＝8-10

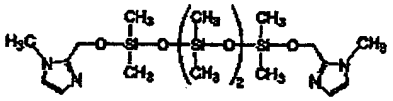
1-3  n＝3-6

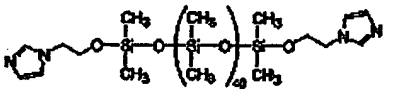
1-4 

[0039] ＊＊【化14】

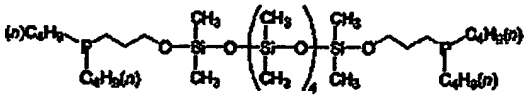
1-5 

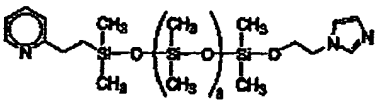
1-6 

1-7 

1-8 

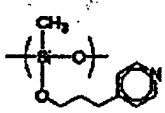
[0040] ※※【化15】

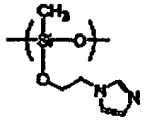
1-9 

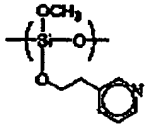
1-10 

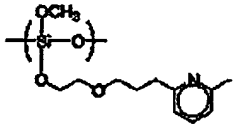
[0041]
【化16】

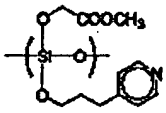
15 16

1-11 

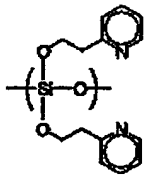
1-12 

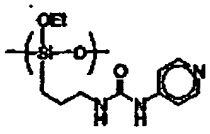
1-13 

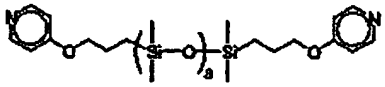
1-14 

1-15 

＊【００４２】
【化17】

1-16 

1-17 

1-18 

【００４３】本発明で用いるシロキサン化合物は、下記一般式(4)により表されるシラン化合物の重合、下記一般式(5)により表される化合物のR_4-H及び／又はR_5-Hによる置換反応、下記一般式(6)により表される化合物とオレフィン化合物とのハイドロシリレーション反応、下記一般式(7)により表される化合物とアルコール化合物との縮合反応等により容易に合成できる。

【００４４】
【化18】

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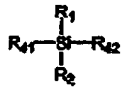
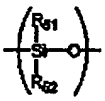


・・・(4)

一般式(4)中、R_{41}及びR_{42}はそれぞれ独立にハロゲン原子又はアルコキシ基を表す。

【００４５】

【化19】

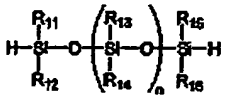


・・・(5)

一般式(5)中、R_{51}及びR_{52}はそれぞれ独立にアルコキシ基又はアリールオキシ基を表す。

【００４６】

【化20】

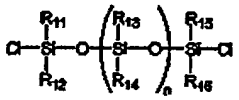


・・・(6)

一般式(6)中のR_{11}～R_{16}及びnは一般式(2)中のそれらと同義であり、好ましい態様も同様である。

【００４７】

【化21】



・・・(7)

一般式(7)中のR_{11}～R_{16}及びnは一般式(2)中のそれらと同義であり、好ましい態様も同様である。

【００４８】(B)求電子剤

本発明の第二の電解質組成物に用いる求電子剤は少なくとも２個の脱離基を有する。該求電子剤は上記シロキサン化合物が有する「求電子剤と反応して共有結合を形成しうる置換基」と反応し、この置換基をアルキル化、オニウム塩化、４級化等することにより直鎖状又は架橋された重合体を形成する。

【００４９】上記シロキサン化合物と求電子剤を反応させて得られる重合体の架橋度を適度なものとするためには、脱離基の数は２～４個であるのが好ましく、２個であるのが特に好ましい。脱離基の数が多いと架橋度が高くなり、その結果、膜質が硬くなりイオン伝導度が低下する。また、脱離基が脱離して生じるアニオンの共役酸のpKaは10以下であるのが好ましく、５以下であるのがより好ましい。

【００５０】脱離基はそれぞれハロゲン原子、アルキルスルホニルオキシ基、アリールスルホニルオキシ基、アシルオキシ基等であってよい。中でもハロゲン原子、アルキルスルホニルオキシ基及びアリールスルホニルオキシ基が好ましい。ハロゲン原子としては、ヨウ素原子、臭素原子及び塩素原子が好ましく、ヨウ素原子及び臭素原子がより好ましい。アルキルスルホニルオキシ基としては、メチルスルホニルオキシ基、クロロメチルスルホニルオキシ基及びパーフルオロアルキルスルホニルオキシ基（トリフルオロメチルスルホニルオキシ基等）が好ましい。アリールスルホニルオキシ基としては、ベンゼンスルホニルオキシ基、p-トルエンスルホニルオキシ基、p-クロロベンゼンスルホニルオキシ基及びp-ニトロベンゼンスルホニルオキシ基が好ましい。アシルオキシ基としては、水素原子の全部若しくは一部をフッ素置換したアルキルカルボニルオキシ基（トリフルオロメチルカルボニルオキシ基等）及びアリールカルボニルオキシ基（p-フルオロフェニルカルボニルオキシ基等）が好ましい。

【００５１】求電子剤の使用量は上記シロキサン化合物との反応速度、或いは生成する重合体の分子量又は架橋度に応じて任意に定めることができる。求電子剤の使用量は、シロキサン化合物が有する「求電子剤と反応して共有結合を形成しうる置換基」のモル数に対して好ましくは0.01～２当量、より好ましくは0.05～1.5当量、特に好ましくは0.1～１当量である。シロキサン化合物が有する求電子剤と反応して共有結合を形成しうる置換基のモル数が明確でない場合は、シロキサン化合物の質量に対する求電子剤の質量比は好ましくは１～100質量%であり、より好ましくは３～70質量%である。求電子剤は単独で用いても２種以上を併用してもよい。以下、本発明で使用可能な求電子剤の具体例E-1～E-27を示すが、本発明はそれらに限定されるものではない。

【００５２】

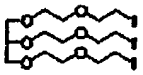
【化22】

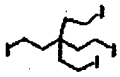
E-1 

E-2 

E-3 

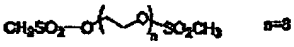
E-4 

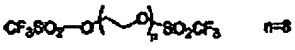
E-5 

E-6 

E-7 

E-8 

E-9 

E-10 

【００５３】

【化23】

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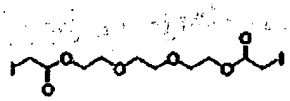
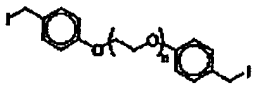
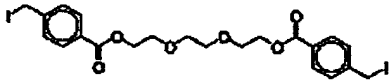
21 22

E-11 

E-12 

E-13 

E-14 

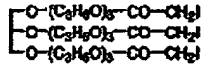
E-15 

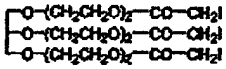
E-16 

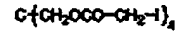
E-17 

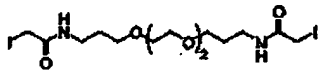
[0054]

＊ ＊ [化24]

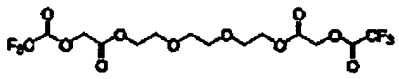
E-18 

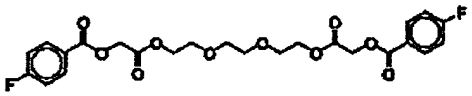
E-19 

E-20 

E-21 

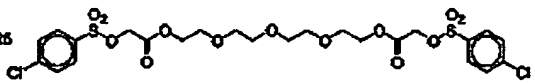
E-22 

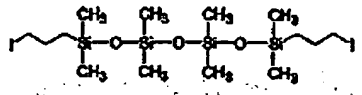
E-23 

E-24 

[0055]

[化25]

E-26 

E-28 

E-27 

【0056】(C)重合反応
本発明の第二の電解質組成物に用いる重合体は、上記求電子剤とシロキサン化合物の重合反応により得ることができる。詳しくは、求電子剤中の求電子部位と、シロキサン化合物中の該求電子剤と反応して共有結合を形成しうる置換基との間で起こるアルキル化反応、オニウム塩を形成する反応（例えば窒素の4級化反応）等により、それらを重合させる。得られる重合体の質量平均分子量は1000～100万であるのが好ましく、2000～50万であるのがより好ましい。

【0057】重合反応は求電子剤及びシロキサン化合物の他に、後述する電解質塩が共存する条件下で行うのが好ましい。反応後に電解質塩を添加してもよいが、この場合、重合体中に電解質塩を均一に分散させるのが困難であり好ましくない。

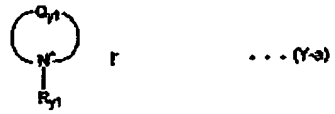
【0058】シロキサン化合物、求電子剤及び電解質塩を含む反応溶液を調製して重合反応を行う場合、シロキサン化合物の質量比は［シロキサン化合物＋電解質塩＋溶媒］を100質量%とすると、1～50質量%とするのが好ましく、3～30質量%とするのがより好ましい。シロキサン化合物が1質量%未満であると流動性が不充分となり、また60質量%を超えるとキャリア移動度が低下するので好ましくない。なお、シロキサン化合物は単独で用いても2種以上を併用してもよい。

【0059】(D)電解質塩
電解質塩としては、例えば(a)I_2とヨウ化物（LiI、NaI、KI、CsI、CaI_2等の金属ヨウ化物、テトラアルキルアンモニウムヨーダイド、ピリジニウムヨーダイド、イミダゾリウムヨーダイド等の4級アンモニウムヨウ素塩等）との組み合わせ、(b)Br_2と臭化物（LiBr、NaBr、KBr、CsBr、$CaBr_2$等の金属臭化物、テトラアルキルアンモニウムブロマイド、ピリジニウムブロマイド等の4級アンモニウム臭素塩等）との組み合わせ、(c)金属錯体（フェロシアン酸塩－フェリシアン酸塩やフェロセン－フェリシニウムイオン等）、(d)イオウ化合物（ポリ硫化ナトリウム、アルキルチオール－アルキルジスルフィド等）、(e)ビオロゲン色素やヒドロキノン－キノン等を用いることができる。中でも、I_2と4級アンモニウムヨウ素塩との組み合わせが好ましい。電解質塩は混合して用いてもよい。

【0060】また、電解質塩としてEP718288、WO95/18456、J. Electrochem. Soc., Vol.143, No.10, 3099 (1996)、Inorg. Chem., 35, 1168～1178 (1996)、特開平8-259543号、電気化学、第65巻、11号、923頁（1997年）等に記載されているピリジニウム塩、イミダゾリウム塩、トリアゾリウム塩等の溶融塩を使用することもできる。溶融塩電解質は耐久性及び電荷輸送能の両立という観点から特に好ましい。なお、ここでいう溶融塩とは室温において液状であるか、又は低融点の塩であり、その融点は100℃以下であるのが好ましく、室温付近であるのが特に好ましい。

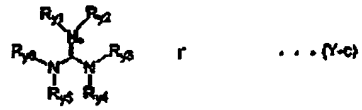
【0061】本発明で好ましく用いることのできる溶融塩としては、下記一般式(Y-a)、(Y-b)及び(Y-c)のいずれかにより表されるものが挙げられる。

【0062】
【化26】



(Y-a)

(Y-b)



(Y-c)

【0063】一般式(Y-a)中、Q_{y1}は窒素原子と共に5又は6員環の芳香族カチオンを形成する原子団を表す。Q_{y1}は炭素原子、水素原子、窒素原子、酸素原子及び硫黄原子からなる群から選ばれる1種以上の原子により構成されるのが好ましい。

【0064】Q_{y1}により形成される5員環は、オキサゾール環、チアゾール環、イミダゾール環、ピラゾール環、イソオキサゾール環、チアジアゾール環、オキサジアゾール環、トリアゾール環、インドール環又はピロー

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ル環であるのが好ましく．オキサゾール環、チアゾール環又はイミダゾール環であるのがより好ましく．オキサゾール環又はイミダゾール環であるのが特に好ましい。Q_1により形成される６員環は．ピリジン環．ピリミジン環．ピリダジン環、ピラジン環又はトリアジン環であるのが好ましく．ピリジン環であるのがより好ましい。

【００６５】一般式(Y-b)中、A_1は窒素原子又はリン原子を表す。

【００６６】一般式(Y-a)、(Y-b)及び(Y-c)中のR_{11}～R_{16}はそれぞれ独立に置換又は無置換のアルキル基（好ましくは炭素原子数１～24．直鎖状であっても分岐状であっても、また環式であってもよく、例えばメチル基、エチル基、プロピル基、イソプロピル基．ペンチル基、ヘキシル基、オクチル基、2-エチルヘキシル基、t-オクチル基．デシル基．ドデシル基、テトラデシル基．2-ヘキシルデシル基．オクタデシル基、シクロヘキシル基、シクロペンチル基等）、或いは置換又は無置換のアルケニル基（好ましくは炭素原子数２～24．直鎖状であっても分岐状であってもよく、例えばビニル基、アリル基等）を表し、より好ましくは炭素原子数２～18のアルキル基又は炭素原子数２～18のアルケニル基であり、特に好ましくは炭素原子数２～６のアルキル基である。

【００６７】また、一般式(Y-b)中のR_{11}～R_{14}のうち２つ以上が互いに連結してA_1を含む非芳香族環を形成してもよく、一般式(Y-c)中のR_{11}～R_{16}のうち２つ以上が互いに連結して環構造を形成してもよい。

【００６８】一般式(Y-a)、(Y-b)及び(Y-c)中のQ_1及びR_{11}～R_{16}は置換基を有していてもよい。この置換基の好ましい例としては、ハロゲン原子（F、Cl．Br、I等）、シアノ基、アルコキシ基（メトキシ基．エトキシ基、メトキシエトキシ基、メトキシエトキシエトキシ基等）、アリーロキシ基（フェノキシ基等）．アルキルチオ基（メチルチオ基．エチルチオ基等）．アルコキシカルボニル基（エトキシカルボニル基等）．炭酸エステル基（エトキシカルボニルオキシ基等）．アシル基（アセチル基．プロピオニル基、ベンゾイル基等）、スルホニル基（メタンスルホニル基．ベンゼンスルホニル基等）、アシルオキシ基（アセトキシ基、ベンゾイルオキシ基等）．スルホニルオキシ基（メタンスルホニルオキシ基．トルエンスルホニルオキシ基等）．ホスホニル基（ジエチルホスホニル基等）、アミド基（アセチルアミノ基．ベンゾイルアミノ基等）、カルバモイル基（N,N-ジメチルカルバモイル基等）、アルキル基（メチル基、エチル基、プロピル基、イソプロピル基、シクロプロピル基．ブチル基．2-カルボキシエチル基、ベンジル基等）．アリール基（フェニル基、トルイル基等）．複素環基（ピリジル基、イミダゾリル基．フラニル基等）、アルケニル基（ビニル基．1-プロペニル基等）．シリル基．シリルオキシ基等が挙げられる。

【００６９】上記一般式(Y-a)～(Y-c)のいずれかにより表される溶融塩は、Q_1及びR_{11}～R_{16}のいずれかを介して多量体を形成してもよい。

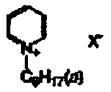
【００７０】上記一般式(Y-a)～(Y-c)のいずれかにより表される溶融塩は単独で使用しても２種以上混合して使用してもよく．またヨウ化物イオンI^-を他のアニオンで置き換えた塩と混合して使用してもよい。I^-を置き換えるアニオンとしては、ハロゲン化物イオン（Cl^-、Br^-等）、SCN^-、BF_4^-．PF_6^-、ClO_4^-、$(CF_3SO_2)_2N^-$、$(CF_3CF_2SO_2)_2N^-$．$CF_3SO_3^-$、$CH_3SO_3^-$．CF_3COO^-、Ph_4B^-、$(CF_3SO_2)_3C^-$等が好ましい。より好ましくはSCN^-、BF_4^-．$CF_3SO_3^-$、CF_3COO^-又は$(CF_3SO_2)_2N^-$である。

【００７１】また、LiIのような他のヨウ素塩やCF_3COOLi、CF_3COONa、LiSCN、NaSCN等のアルカリ金属塩を添加することもできる。アルカリ金属塩の添加量は．0.02～２質量%程度とするのが好ましく、0.1～１質量%とするのが更に好ましい。

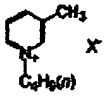
【００７２】本発明で好ましく用いられる電解質塩の具体例(Y1)～(Y29)を以下に挙げるが、それらは本発明を限定するものではない。

【００７３】

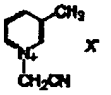
【化27】

(Y1) 

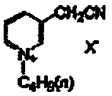
Y1-1 : X⁻=I⁻
Y1-2 : X⁻=BF_4^-
Y1-3 : X⁻=$N(SO_2CF_3)_2^-$
Y1-4 : X⁻=PF_6^-

(Y2) 

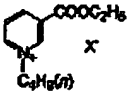
Y2-1 : X⁻=I⁻
Y2-2 : X⁻=BF_4^-
Y2-3 : X⁻=$N(SO_2CF_3)_2^-$
Y2-4 : X⁻=CF_3COO^-
Y2-5 : X⁻=SCN^-
Y2-6 : X⁻=$CF_3SO_3^-$

(Y3) 

Y3-1 : X⁻=I⁻
Y3-2 : X⁻=BF_4^-
Y3-3 : X⁻=$N(SO_2CF_3)_2^-$

(Y4) 

Y4-1 : X⁻=I⁻
Y4-2 : X⁻=BF_4^-
Y4-3 : X⁻=$N(SO_2CF_3)_2^-$

(Y5) 

Y5-1 : X⁻=I⁻
Y5-2 : X⁻=BF_4^-
Y5-3 : X⁻=$N(SO_2CF_3)_2^-$

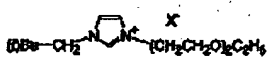
(Y6) 

Y6-1 : X⁻=I⁻
Y6-2 : X⁻=BF_4^-
Y6-3 : X⁻=$N(SO_2CF_3)_2^-$
Y6-4 : X⁻=Br^-
Y6-5 : X⁻=CF_3COO^-
Y6-6 : X⁻=SCN^-
Y6-7 : X⁻=$CF_3SO_3^-$

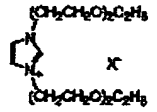
【００７４】 【化28】

(Y7) 

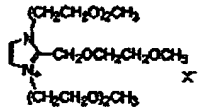
Y7-1 : X⁻=I⁻
Y7-2 : X⁻=BF_4^-
Y7-3 : X⁻=$N(SO_2CF_3)_2^-$
Y7-4 : X⁻=CF_3COO^-
Y7-5 : X⁻=SCN^-

(Y8) 

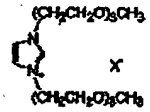
Y8-1 : X⁻=I⁻
Y8-2 : X⁻=BF_4^-
Y8-3 : X⁻=$N(SO_2CF_3)_2^-$
Y8-4 : X⁻=PF_6^-
Y8-5 : X⁻=CF_3COO^-
Y8-6 : X⁻=SCN^-
Y8-7 : X⁻=$CF_3SO_3^-$

(Y9) 

Y9-1 : X⁻=I⁻
Y9-2 : X⁻=BF_4^-
Y9-3 : X⁻=$N(SO_2CF_3)_2^-$
Y9-4 : X⁻=CF_3COO^-
Y9-5 : X⁻=SCN^-
Y9-6 : X⁻=$CF_3SO_3^-$

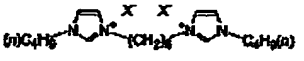
(Y10) 

Y10-1 : X⁻=I⁻
Y10-2 : X⁻=BF_4^-
Y10-3 : X⁻=$N(SO_2CF_3)_2^-$

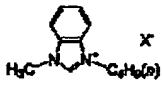
(Y11) 

Y11-1 : X⁻=I⁻
Y11-2 : X⁻=BF_4^-
Y11-3 : X⁻=$N(SO_2CF_3)_2^-$

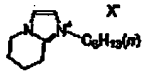
【0075】 ＊＊【化29】

(Y12) 

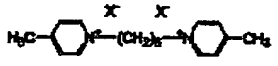
Y12-1 : X⁻=I⁻
Y12-2 : X⁻=BF_4^-
Y12-3 : X⁻=$N(SO_2CF_3)_2^-$

(Y13) 

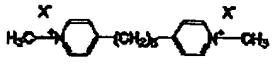
Y13-1 : X⁻=I⁻
Y13-2 : X⁻=BF_4^-
Y13-3 : X⁻=$N(SO_2CF_3)_2^-$

(Y14) 

Y14-1 : X⁻=I⁻
Y14-2 : X⁻=BF_4^-
Y14-3 : X⁻=$N(SO_2CF_3)_2^-$

(Y15) 

Y15-1 : X⁻=I⁻
Y15-2 : X⁻=BF_4^-
Y15-3 : X⁻=$N(SO_2CF_3)_2^-$

(Y16) 

Y16-1 : X⁻=I⁻
Y16-2 : X⁻=BF_4^-
Y16-3 : X⁻=$N(SO_2CF_3)_2^-$

【0076】 【化30】

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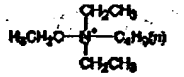
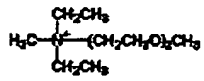
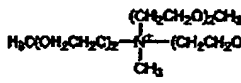
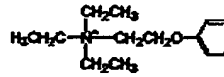
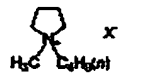
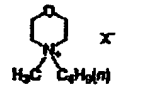
(Y17)  Y17-1：X⁻＝I⁻ Y17-2：X⁻＝BF_4^- Y17-3：X⁻＝$N(SO_2CF_3)_2^-$ Y17-4：X⁻＝PF_6^-

(Y18)  Y18-1：X⁻＝I⁻ Y18-2：X⁻＝BF_4^- Y18-3：X⁻＝$N(SO_2CF_3)_2^-$

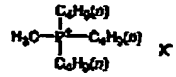
(Y19)  Y19-1：X⁻＝I⁻ Y19-2：X⁻＝BF_4^- Y19-3：X⁻＝$N(SO_2CF_3)_2^-$ Y19-4：X⁻＝CF_3COO^- Y19-5：X⁻＝SCN^- Y19-6：X⁻＝$CF_3SO_3^-$

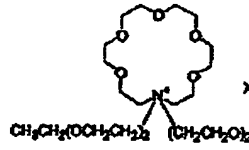
(Y20)  Y20-1：X⁻＝I⁻ Y20-2：X⁻＝BF_4^- Y20-3：X⁻＝$N(SO_2CF_3)_2^-$

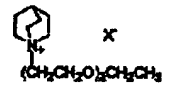
(Y21)  Y21-1：X⁻＝I⁻ Y21-2：X⁻＝BF_4^- Y21-3：X⁻＝$N(SO_2CF_3)_2^-$

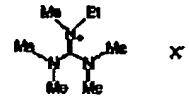
(Y22)  Y22-1：X⁻＝I⁻ Y22-2：X⁻＝BF_4^- Y22-3：X⁻＝$N(SO_2CF_3)_2^-$

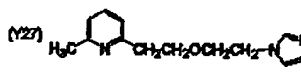
[0077] ＊＊[化31]

(Y23)  Y23-1：X⁻＝I⁻ Y23-2：X⁻＝BF_4^- Y23-3：X⁻＝$N(SO_2CF_3)_2^-$

(Y24)  Y24-1：X⁻＝I⁻ Y24-2：X⁻＝BF_4^- Y24-3：X⁻＝$N(SO_2CF_3)_2^-$

(Y25)  Y25-1：X⁻＝I⁻ Y25-2：X⁻＝BF_4^- Y25-3：X⁻＝$N(SO_2CF_3)_2^-$

(Y26)  Y26-1：X⁻＝I⁻ Y26-2：X⁻＝$N(SO_2CF_3)_2^-$ Y26-3：X⁻＝BF_4^- Y26-4：X⁻＝PF_6^-

(Y27)  Y27-1：X⁻＝I⁻ Y27-2：X⁻＝$N(SO_2CF_3)_2^-$ Y27-3：X⁻＝BF_4^- Y27-4：X⁻＝CF_3COO^- Y27-5：X⁻＝SCN^- Y27-6：X⁻＝$CF_3SO_3^-$

[0078] [化32]

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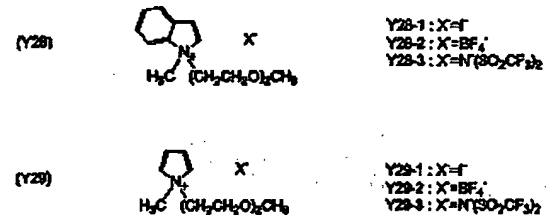


【００７９】本発明では．電解質塩として常温で溶融状態であるものを用い、溶媒を使用しないのが好ましい。後述する溶媒を添加しても構わないが．電解質塩の含有量は電解質組成物全体に対して50質量%以上であるのが好ましく、90質量%以上であるのが特に好ましい。また．本発明の第一及び第二の電解質組成物は、上記シロキサン化合物及び上記塩合体以外のヨウ素塩を含有するのが好ましく．用いる塩のうち50質量%以上がヨウ素塩であることが好ましい。また、溶媒を使用する場合は、電解質塩の濃度を0.05～２mol/lとするのが好ましく．0.1～1.5mol/lとするのがより好ましい。

【００８０】(E)ヨウ素

本発明の第一及び第二の電解質組成物はヨウ素を含有するのが好ましい。ヨウ素含有量は電解質組成物全体に対して0.1～20質量%であるのが好ましく、0.5～５質量%であるのがより好ましい。また、前述したシロキサン化合物．求電子剤及び電解質塩を含む反応溶液にヨウ素や臭素を添加して酸化還元対を予め生成させておくこともできる。この反応溶液中のヨウ素又は臭素の濃度は0.01～0.3mol/lとするのが好ましい。

【００８１】(F)溶媒

本発明の第一及び第二の電解質組成物は溶媒を含んでいてもよい。電解質組成物の溶媒含有量は全体の50質量%以下であるのが好ましく．30質量%以下であるのがより好ましく、10質量%以下であるのが特に好ましい。

【００８２】溶媒としては．低粘度でイオン移動度が高いか．高誘電率で有効キャリア濃度を高めるか．或いはその両方であるために、優れたイオン伝導性を発現できるものが好ましい。このような溶媒として、カーボネート化合物（エチレンカーボネート、プロピレンカーボネート等）、複素環化合物（3-メチル-2-オキサゾリジノン等）、エーテル化合物（ジオキサン．ジエチルエーテル等）、鎖状エーテル類（エチレングリコールジアルキルエーテル、プロピレングリコールジアルキルエーテル．ポリエチレングリコールジアルキルエーテル．ポリプロピレングリコールジアルキルエーテル等）．アルコール類（メタノール、エタノール、エチレングリコールモノアルキルエーテル、プロピレングリコールモノアルキルエーテル．ポリエチレングリコールモノアルキルエーテル、ポリプロピレングリコールモノアルキルエーテル等）、多価アルコール類（エチレングリコール．プロピレングリコール、ポリエチレングリコール、ポリプロピレングリコール、グリセリン等）．ニトリル化合物（アセトニトリル、グルタロジニトリル、メトキシアセトニトリル、プロピオニトリル、ベンゾニトリル．ビスシアノエチルエーテル等）．エステル類（カルボン酸エステル、リン酸エステル．ホスホン酸エステル等）、非プロトン性極性溶媒（ジメチルスルホキシド（DMSO）、スルフォラン等）、水等が挙げられる。中でも．カーボネート化合物．ニトリル化合物、複素環化合物が好ましい。これらの溶媒は必要に応じて二種以上を混合して用いてもよい。

【００８３】(G)その他

本発明の第一及び第二の電解質組成物には、J. Am. Ceram. Soc., 80(12), 3157-3171 (1997)等に記載のt-ブチルピリジン、2-ピコリン．2,6-ルチジン等の塩基性化合物を添加するのが好ましい。塩基性化合物を添加する場合の好ましい濃度範囲は0.05～２Mである。

【００８４】第一及び第二の電解質組成物をゲル化するために、ポリマー添加、オイルゲル化剤添加、多官能モノマーを含むモノマー類の重合、ポリマーの架橋反応等の手法を併用できる。ポリマー添加によりゲル化させる場合は、"Polymer Electrolyte Reviews-１及び２"（J. R. MacCallumとC. A. Vincentの共編、ELSEVIER APPLIED SCIENCE）に記載の化合物等が使用可能であり、ポリアクリロニトリル又はポリフッ化ビニリデンを用いるのが好ましい。オイルゲル化剤添加によりゲル化させる場合はJ. Chem. Soc. Japan, Ind. Chem.Sec., 46, 779 (1943). J. Am. Chem. Soc., 111, 5542 (1989), J. Chem. Soc., Chem. Commun., 1993, 390. Angew. Chem. Int. Ed. Engl., 35, 1949 (1996). Chem. Lett., 1996, 885, J. Chem. Soc., Chem. Commun., 1997, 545等に記載されている化合物を使用することができ．アミド構造を有する化合物を用いるのが好ましい。また、特開平11-185863に記載の電解液のゲル化法．及び特開2000-58140に記載の溶融塩電解質のゲル化法も．本発明に適用できる。また、ポリマーの架橋反応により電解質組成物をゲル化させる場合．特開2000-17076、同2000-86724に記載されている架橋技術も適用できる。

【００８５】[2]光電変換素子

本発明の光電変換素子は導電層、感光層、電荷輸送層及び対極を有する。好ましくは図１に示すように．導電層10．下塗り層60．感光層20．電荷輸送層30、対極導電層40の順に積層し．感光層20を色素22によって増感された

半導体微粒子21と当該半導体微粒子21の間の空隙に浸透した電荷輸送材料23とから構成する。電荷輸送材料23は、電荷輸送層30に用いる材料と同じ成分からなる。また光電変換素子に強度を付与するため、導電層10及び／又は対極導電層40の下地として基板50を設けてもよい。本発明では、導電層10及び任意で設ける基板50からなる層を「導電性支持体」、対極導電層40及び任意で設ける基板50からなる層を「対極」と呼ぶ。なお、図１中の導電層10、対極導電層40、基板50は、それぞれ透明導電層10a、透明対極導電層40a、透明基板50aであってもよい。この光電変換素子を外部負荷に接続して電気的仕事（発電）をさせるものが光電池であり、光学的情報のセンシングを目的に作られたものが光センサーである。

【００８６】図１に示す本発明の光電変換素子において、半導体微粒子がn型である場合、色素22により増感された半導体微粒子21を含む感光層20に入射した光は色素22を励起し、励起された色素22中の高エネルギーの電子が半導体微粒子21の伝導帯に渡され、更に拡散により導電層10に到達する。このとき、色素22は酸化体となっている。光電池においては、導電層10中の電子が外部回路で仕事をしながら対極導電層40及び電荷輸送層30を経て色素22の酸化体に戻り、色素22が再生する。感光層20は負極（光アノード）として働き、対極40は正極として働く。それぞれの層の境界（例えば導電層10と感光層20との境界、感光層20と電荷輸送層30との境界、電荷輸送層30と対極導電層40との境界等）では、各層の構成成分同士が相互に拡散混合していてもよい。以下、各層について詳細に説明する。

【００８７】(A)導電性支持体

導電性支持体は(1)導電層の単層、又は(2)導電層及び基板の２層からなる。(1)の場合は、導電層の材料として強度及び密封性が十分に保たれるようなものを使用し、例えば金属材料（白金、金、銀、銅、亜鉛、チタン、アルミニウム、これらの合金等）を用いることができる。(2)の場合、感光層側に導電剤を含有する導電層を有する基板を使用することができる。好ましい導電剤としては金属（例えば白金、金、銀、銅、亜鉛、チタン、アルミニウム、インジウム、これらを含む合金等）、炭素及び導電性金属酸化物（インジウムースズ複合酸化物、酸化スズにフッ素又はアンチモンをドープしたもの等）が挙げられる。導電層の厚さは0.02～10μm程度が好ましい。

【００８８】導電性支持体は表面抵抗が低い程よい。表面抵抗は好ましくは50Ω/□以下であり、より好ましくは20Ω/□以下である。

【００８９】導電性支持体側から光を照射する場合には、導電性支持体は実質的に透明であるのが好ましい。実質的に透明であるとは、可視～近赤外領域（400～1200nm）の一部又は全域において光透過率が10%以上であることを意味する。この光透過率は50%以上であるのが好ましく、80%以上であるのがより好ましい。特に、感光層が感度を有する波長域の光透過率が高いことが好ましい。

【００９０】透明導電性支持体としては、ガラスやプラスチック等の透明基板の表面に導電性金属酸化物からなる透明導電層を塗布又は蒸着等により形成したものが好ましい。透明導電層はフッ素又はアンチモンをドーピングした二酸化スズ、或いはインジウムースズ酸化物（ITO）からなるのが好ましい。透明基板としてはコストと強度の点で有利なソーダガラス、アルカリ溶出の影響のない無アルカリガラス等のガラス基板に加え、透明ポリマーフィルムが使用可能である。透明ポリマーフィルムの材料としては、トリアセチルセルロース（TAC）、ポリエチレンテレフタレート（PET）、ポリエチレンナフタレート（PEN）、シンジオタクチックポリスチレン（SPS）、ポリフェニレンスルフィド（PPS）、ポリカーボネート（PC）、ポリアリレート（PAr）、ポリスルフォン（PSF）、ポリエステルスルフォン（PES）、ポリイミド（PI）、ポリエーテルイミド（PEI）、環状ポリオレフィン、ブロム化フェノキシ等が使用可能である。十分な透明性を確保するために、導電性金属酸化物の塗布量はガラス又はプラスチックの支持体１㎡当たり0.01～100gとするのが好ましい。

【００９１】透明導電性支持体の抵抗を下げる目的で金属リードを用いるのが好ましい。金属リードの材質は白金、金、ニッケル、チタン、アルミニウム、銅、銀等の金属が好ましい。金属リードは透明基板に蒸着、スパッタリング等で設置し、その上に導電性の酸化スズ又はITOからなる透明導電層を設けるのが好ましい。金属リード設置による入射光量の低下は好ましくは10%以内、より好ましくは１～５%に抑える。

【００９２】(B)感光層

(1)半導体

感光層は色素によって増感された半導体微粒子を含有するのが好ましい。感光層において半導体は感光体として作用し、光を吸収して電荷分離を行い電子と正孔を生ずる。色素増感された半導体では、光吸収及びこれによる電子及び正孔の発生は主として色素において起こり、半導体はこの電子（又は正孔）を受け取り、伝達する役割を担う。本発明で用いる半導体は光励起下で伝導帯電子がキャリアとなりアノード電流を与えるn型半導体であることが好ましい。

【００９３】本発明で用いる半導体の例としては、シリコンやゲルマニウムのような単体半導体、III-V系化合物半導体、金属のカルコゲナイド（酸化物、硫化物、セレン化物、それらの複合物等）、ペロブスカイト構造を有する化合物（チタン酸ストロンチウム、チタン酸カルシウム、チタン酸ナトリウム、チタン酸バリウム、ニオブ酸カリウム等）等が挙げられる。中でも金属カルコゲナイドが好ましい。

【００９４】好ましい金属カルコゲナイドとして．チタン．スズ、亜鉛．鉄、タングステン．ジルコニウム、ハフニウム、ストロンチウム．インジウム、セリウム、イットリウム、ランタン、バナジウム．ニオブ又はタンタルの酸化物、カドミウム．亜鉛、鉛．銀、アンチモン又はビスマスの硫化物、カドミウム又は鉛のセレン化物、カドミウムのテルル化物等が挙げられる。他の化合物半導体としては亜鉛、ガリウム、インジウム、カドミウム等のリン化物．ガリウム－ヒ素又は銅－インジウムのセレン化物、銅－インジウムの硫化物等が挙げられる。更に．M_1O_x、$M_1M_2O_x$や$M_1M_2M_3O_x$（M_1、M_2及びM_3はそれぞれ金属原子．Oは酸素原子、x、y及びzは価数が中性になる数を表す）のような複合物も好ましく用いることができる。

【００９５】本発明で用いる半導体は．好ましくはSi、TiO_2．SnO_2、Fe_2O_3．WO_3．ZnO．Nb_2O_5．CdS．ZnS．PbS．Bi_2S_3、CdSe．CdTe、$SrTiO_3$、GaP、InP、GaAs．CuInS$_2$又はCuInSe$_2$であり．より好ましくはTiO_2．SnO_2、Fe_2O_3．WO_3．ZnO．Nb_2O_5．CdS．PbS．CdSe、$SrTiO_3$、InP、GaAs．CuInS$_2$又はCuInSe$_2$であり．特に好ましくはTiO_2又はNb_2O_5であり、最も好ましくはTiO_2である。TiO_2はアナターゼ型結晶を70%以上含むのが好ましく．100%アナターゼ型結晶であるのがより好ましい。

【００９６】半導体中の電子電導性を上げる目的で金属をドープするのが好ましい。ドープする金属としては2価又は3価の金属が好ましい。半導体から電荷輸送層へ逆電流が流れるのを防止するために半導体に１価の金属をドープするのも有効である。

【００９７】本発明に用いる半導体は単結晶でも多結晶でもよいが、製造コスト．原材料確保及びエネルギーペイバックタイムの観点からは多結晶が好ましい。一部アモルファス部分を含んでいてもよい。半導体は半導体微粒子からなる多孔質膜として用いるのが好ましい。

【００９８】半導体微粒子の粒径は一般にnm～μmのオーダーである。微粒子の投影面積を円に換算したときの直径から求めた一次粒子平均粒径は5～200nmであるのが好ましく、8～100nmであるのがより好ましい。また．導電性支持体上に塗布するために作製する分散液中の半導体微粒子（二次粒子）の平均粒径は0.01～30μmであるのが好ましい。粒径分布の異なる２種類以上の微粒子を混合してもよく、この場合小さい粒子の平均サイズは25nm以下であるのが好ましく、10nm以下であるのがより好ましい。入射光を散乱させて光捕獲率を向上させる目的で、粒径の大きな．例えば100nm以上．300nm程度の半導体粒子を混合することも好ましい。

【００９９】種類も異なる２種以上の半導体微粒子を混合して用いてもよい。このような場合．１種はTiO_2、ZnO、Nb_2O_5又は$SrTiO_3$であることが好ましい。もう一方はSnO_2．Fe_2O_3又はWO_3であるのが好ましい。中でも．ZnOとSnO_2、ZnOとWO_3、或いはZnO又はSnO_2とWO_3の組み合わせがより好ましい。２種以上の半導体微粒子を混合して用いる場合、それぞれの粒径は異なっていてもよい。特に上記TiO_2、ZnO、Nb_2O_5又は$SrTiO_3$の粒径は大きく、SnO_2．Fe_2O_3又はWO_3の粒径は小さいのが好ましい。粒径が100nm以上の大きい粒子と粒径が15nm以下の小さい粒子の組み合わせが好ましい。

【０１００】半導体微粒子の作製法としては、作花済夫の「ゾルーゲル法の科学」アグネ承風社（1998年）、技術情報協会の「ゾルーゲル法による薄膜コーティング技術」（1995年）等に記載のゾルーゲル法、杉本忠夫の「新合成法ゲルーゾル法による単分散粒子の合成とサイズ形態制御」．まてりあ、第35巻，第９号，1012～1018頁（1996年）等に記載のゲルーゾル法が好ましい。また．Degussa社が開発した塩化物を酸水素塩中で高温加水分解により酸化物を作製する方法も好ましく適用できる。

【０１０１】半導体微粒子が酸化チタンの場合．上記ゾル-ゲル法．ゲルーゾル法、塩化物の酸水素塩中での高温加水分解法はいずれも好ましく利用でき、更に清野学の「酸化チタン　物性と応用技術」技報堂出版（1997年）に記載の硫酸法及び塩素法を用いてもよい。加えて．Barbeらのジャーナル・オブ・アメリカン・セラミック・ソサエティー，第80巻，第12号．3157～3171頁（1997年）、Burnsideらのケミカル・マテリアルズ，第10巻．第９号．2419～2425頁等に記載のゾルーゲル法も好ましい。

【０１０２】(2)半導体微粒子層

半導体微粒子を導電性支持体上に塗布する際には．半導体微粒子の分散液又はコロイド溶液を導電性支持体上に塗布する方法に加え、前述のゾル-ゲル法等を使用することができる。光電変換素子の量産化．半導体微粒子分散液の物性、導電性支持体の融通性等を考慮すると、湿式製膜方法が比較的好ましい。湿式製膜方法としては塗布法．印刷法．電解析出法及び電着法が代表的である。また．金属を酸化する方法．金属溶液から配位子交換等で液相にて析出させる方法（LPD法）、スパッタ等で蒸着する方法、CVD法．或いは加温した基板上に熱分解する金属酸化物プレカーサーを吹き付けて金属酸化物を形成するSPD法を用いてもよい。

【０１０３】半導体微粒子の分散液を作製する方法としては．前述のゾル-ゲル法、乳鉢ですり潰す方法、ミルを使って粉砕しながら分散する方法．半導体を合成する際に溶媒中で微粒子として析出させそのまま使用する方法等が挙げられる。

【０１０４】分散媒としては、水又は各種の有機溶媒（例えばメタノール、エタノール、イソプロピルアルコール．シトロネロール、ターピネオール、ジクロロメタン．アセトン．アセトニトリル、酢酸エチル等）が使用可能である。分散する際には、必要に応じてポリエチレングリコール．ヒドロキシエチルセルロース、カルボキシメチルセルロース等のポリマー、界面活性剤．酸、キ

レート剤等を分散助剤として用いてよい。中でも、ポリエチレングリコールを添加するのが好ましい。添加するポリエチレングリコールの分子量を変えることにより分散液の粘度が調節でき、割れにくい半導体層を形成したり、半導体層の空隙率をコントロールできる。

【0105】好ましい塗布方法としては、ローラ法、ディップ法等のアプリケーション系、エアーナイフ法、ブレード法等のメータリング系、特公昭58-4589号に記載のワイヤーバー法、米国特許2681294号、同2761419号、同2761791号等に記載のスライドホッパー法、エクストルージョン法、カーテン法等のアプリケーションとメータリングを同一部分にできる方法等が挙げられる。また汎用機としてスピン法やスプレー法も好ましい。湿式印刷方法としては、凸版、オフセット及びグラビアの3大印刷法をはじめ、凹版、ゴム版、スクリーン印刷等が好ましく利用できる。以上の方法の中から、液粘度やウェット厚さに応じて好ましい製膜方法を選択すればよい。

【0106】半導体微粒子層は単層に限らず、粒径の異なる半導体微粒子分散液を多層塗布したり、異なる種類の半導体微粒子（或いは異なるバインダー、添加剤等）を含有する層を多層塗布したりすることもできる。一度の塗布では膜厚が不足する場合にも、多層塗布は有効である。

【0107】一般に、半導体微粒子層の厚さ（感光層の厚さと同じ）が厚くなるほど、単位投影面積当たりの色素担持量が増えるため光の捕獲率が高くなるが、生成した電子の拡散距離が増すため電荷再結合によるロスも大きくなる。従って、半導体微粒子層の好ましい厚さは0.1～100μmである。光電池に用いる場合、半導体微粒子層の厚さは1～30μmであるのが好ましく、2～25μmであるのがより好ましい。支持体1m²当たりの半導体微粒子塗布量は0.5～100gとするのが好ましく、3～50gとするのがより好ましい。

【0108】半導体微粒子を導電性支持体に塗布した後、半導体微粒子同士を電子的に接触させると共に塗膜強度や支持体との密着性を向上させるために、加熱処理を施すのが好ましい。加熱温度は40℃以上700℃未満とするのが好ましく、100℃以上600℃以下とするのがより好ましい。また、加熱時間は10分～10時間程度とすればよい。ポリマーフィルムのように融点や軟化点の低い支持体を用いる場合は、高温での加熱処理は支持体の劣化を招くため好ましくない。また、コスト削減の観点からも、加熱処理はできる限り低温（例えば50℃～350℃）で行うのが好ましい。上述した粒径5nm以下の半導体微粒子を併用したり、加熱処理を鉱酸や金属酸化物ブレカーサーの存在下で行うことにより、加熱処理温度の低温化が可能となる。また紫外線、赤外線、マイクロ波等の照射や高圧又は超音波を印加することにより低温化できる。不要な有機物等を除去する目的で、上記の照射等に加えて加熱、減圧、酸素プラズマ処理、純水洗浄、溶剤洗浄、ガス洗浄等を適宜併用するのが好ましい。

【0109】加熱処理後、半導体微粒子の表面積を増大させるため、或いは半導体微粒子近傍の純度を高め色素から半導体微粒子への電子注入効率を高めるために、例えば四塩化チタン水溶液を用いた化学メッキ処理や三塩化チタン水溶液を用いた電気化学的メッキ処理を施してもよい。また、半導体微粒子から電荷輸送層へ逆電流が流れるのを防止するために、粒子表面に色素以外の電子電導性の低い有機物を吸着させるのも有効である。吸着させる有機物は疎水性基を持つのが好ましい。

【0110】半導体微粒子層は多くの色素を吸着することができるように大きな表面積を有するのが好ましい。半導体微粒子を支持体上に塗布した状態での表面積は、投影面積に対して10倍以上であるのが好ましく、100倍以上であるのがより好ましい。上限は特に制限はないが、通常1000倍程度である。

【0111】(3)色素

感光層に使用する色素は可視域や近赤外域に吸収を有し、半導体を増感しうるものであればよく、好ましくは金属錯体色素、メチン色素、ポルフィリン系色素及び／又はフタロシアニン系色素であり、特に好ましくは金属錯体色素及び／又はポリメチン色素である。光電変換の波長域をできるだけ広くし、且つ変換効率を上げるために、二種類以上の色素を併用してもよい。この場合、光源の波長域と強度分布に合わせて、併用する色素とその混合割合を選択すればよい。

【0112】本発明で用いる色素は、好ましくは半導体微粒子表面に対して吸着能力のある適当な結合基（interlocking group）を有する。好ましい結合基としては-COOH基、-OH基、$-SO_3H$基、$-P(O)(OH)_2$基及び$-OP(O)(OH)_2$基のような酸性基、並びにオキシム、ジオキシム、ヒドロキシキノリン、サリチレート及びα-ケトエノレートのようなπ伝導性を有するキレート化基が挙げられる。中でも-COOH基、$-P(O)(OH)_2$基及び$-OP(O)(OH)_2$基が特に好ましい。これらの結合基はアルカリ金属等と塩を形成していてもよく、分子内塩を形成していてもよい。またポリメチン色素においては、メチン鎖がスクアリリウム環やクロコニウム環を形成する場合のように酸性基を含有するなら、この部分を結合基としてもよい。以下、感光層に用いる好ましい増感色素を具体的に説明する。

【0113】(a)金属錯体色素

本発明で使用する金属錯体色素は金属フタロシアニン色素又は金属ポルフィリン色素であるのが好ましい。また、金属錯体色素の金属原子はルテニウムRuが好ましい。本発明で使用できるルテニウム錯体色素としては、例えば米国特許4927721号、同4684537号、同5084365号、同5350644号、同5463057号、同5525440号、特開平7-249790号、特表平10-504512号、世界特許98/50393号、特開2000-26487号等に記載のものが挙げられる。

【0114】本発明で用いるルテニウム錯体色素は下記

一般式(I)：

$(A_1)_pRu(B\text{-}a)(B\text{-}b)(B\text{-}c)$ ・・・(I)

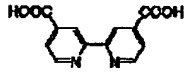
により表されるのが好ましい。一般式(I)中、A_1は１又は２座の配位子を表し、Cl、SCN、H_2O、Br、I、CN、NCO及びSeCN、並びにβ－ジケトン類、シュウ酸及びジチオカルバミン酸の誘導体からなる群から選ばれた配位子を＊

＊表す。pは０～３の整数である。B-a、B-b及びB-cはそれぞれ独立に下記式B-1～B-10により表される化合物から選ばれた有機配位子を表す。

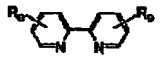
【０１１５】

【化33】

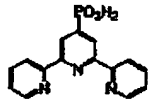
B-1



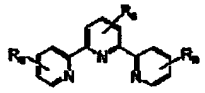
B-2



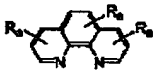
B-3



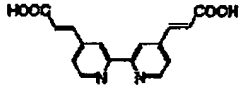
B-4



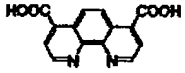
B-5



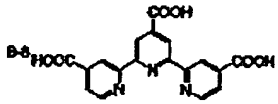
B-6



B-7



B-8



B-9

B-10

【０１１６】式B-1～B-10中、R_aは水素原子又は置換基を表す。該置換基の例としては、ハロゲン原子、炭素原子数１～12の置換又は無置換のアルキル基、炭素原子数７～12の置換又は無置換のアラルキル基、炭素原子数６～12の置換又は無置換のアリール基、上記酸性基（塩を形成していてもよい）やキレート化基が挙げられる。ここで、アルキル基及びアラルキル基のアルキル部分は直鎖状でも分岐状でもよく、またアリール基及びアラルキル基のアリール部分は単環でも多環（縮合環、環集合）でもよい。B-a、B-b及びB-cは同一でも異なっていてもよく、いずれか１つ又は２つでもよい。

【０１１７】本発明で使用できる金属錯体色素の好ましい具体例を以下に示すが、本発明はこれらに限定されるものではない。

【０１１８】

【化34】

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43 44

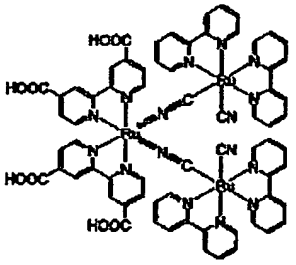
$(A_1)_pRu(B\text{-}a)(B\text{-}b)(B\text{-}c)$ ・・・(1)

	A_1	p	B-a	B-b	B-c	R_a
R-1	SCN	2	B-1	B-1	—	—
R-2	CN	2	B-1	B-1	—	—
R-3	Cl	2	B-1	B-1	—	—
R-4	CN	2	B-7	B-7	—	—
R-5	SCN	2	B-7	B-7	—	—
R-6	SCN	2	B-1	B-2	—	H
R-7	SCN	1	B-1	B-3	—	—
R-8	Cl	1	B-1	B-4	—	H
R-9	I	2	B-1	B-5	—	H
R-10	SCN	3	B-6	—	—	—
R-11	CN	3	B-8	—	—	—
R-12	SCN	1	B-2	B-6	—	H
R-13	—	0	B-1	B-1	B-1	—

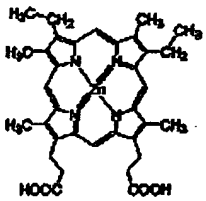
【0119】

＊＊【化35】

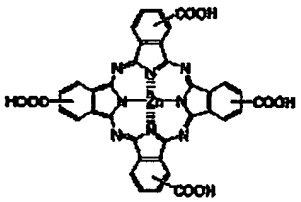
R-14



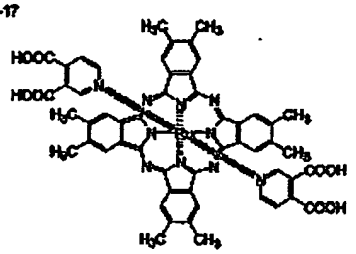
R-15



R-16



R-17



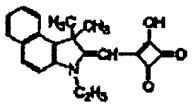
【０１２０】(b)メチン色素

本発明で使用するメチン色素は、好ましくはシアニン色素、メロシアニン色素、スクワリリウム色素等のポリメチン色素である。ポリメチン色素としては特開平11-35836号、特開平11-67285号、特開平11-86916号、特開平11-97725号、特開平11-158395号、特開平11-163378号、特開平11-214730号、特開平11-214731号、特開平11-238905号、特開2000-26487号、欧州特許892411号、同911841号及び同991092号に記載のものが使用できる。好ましいメチン色素の具体例を下に示す。

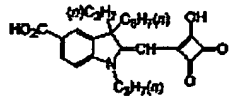
【０１２１】

【化36】

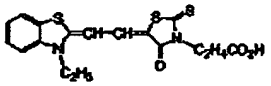
M-1



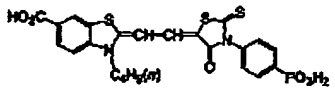
M-2



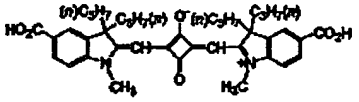
M-3



M-4



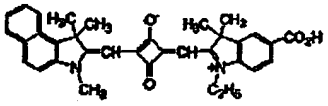
M-5



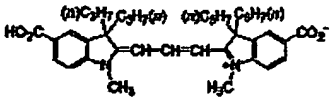
【０１２２】

【化37】

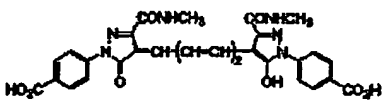
M-6



M-7



M-8



【０１２３】(4)半導体微粒子への色素の吸着

半導体微粒子に色素を吸着させるためには、色素の溶液中によく乾燥した半導体微粒子層を有する導電性支持体を浸漬する方法、或いは色素の溶液を半導体微粒子層に塗布する方法を用いることができる。前者の方法では、浸漬法、ディップ法、ローラ法、エアーナイフ法等が使用可能である。なお、浸漬法の場合、色素の吸着は室温で行ってもよいし、特開平7-249790号に記載されているように加熱還流して行ってもよい。また、後者の方法としては、ワイヤーバー法、スライドホッパー法、エクストルージョン法、カーテン法、スピン法、スプレー法等の塗布方法がある。

【０１２４】色素の溶液に用いる溶媒は色素の溶解性等に応じて適宜選択でき、例えばアルコール類（メタノール、エタノール、t-ブタノール、ベンジルアルコール等）、ニトリル類（アセトニトリル、プロピオニトリル、3-メトキシプロピオニトリル等）、ニトロメタン、ハロゲン化炭化水素（ジクロロメタン、ジクロロエタン、クロロホルム、クロロベンゼン等）、エーテル類（ジエチルエーテル、テトラヒドロフラン等）、ジメチルスルホキシド、アミド類（N,N-ジメチルホルムアミド、N,N-ジメチルアセタミド等）、N-メチルピロリドン、1,3-ジメチルイミダゾリジノン、3-メチルオキサゾリジノン、エステル類（酢酸エチル、酢酸ブチル等）、炭酸エステル類（炭酸ジエチル、炭酸エチレン、炭酸プロピレン等）、ケトン類（アセトン、2-ブタノン、シクロヘキサノン等）、炭化水素（ヘキサン、石油エーテル、ベンゼン、トルエン等）、これらの混合溶媒等が使用できる。

【０１２５】色素の全吸着量は、導電性支持体の単位表面積（１㎡）当たり0.01～100mmolとするのが好ましい。また、色素の半導体微粒子に対する吸着量は、十分な増感効果を得るためには半導体微粒子１g当たり0.01～１mmolであるのが好ましい。色素の吸着量が少なすぎると増感効果が不十分となり、また多すぎると色素が浮遊しやすく、増感効果を低減させる原因となる。また、色素の吸着量を増大させるために吸着前に加熱処理を施すのが好ましい。加熱処理の後に半導体微粒子表面に水が吸着するのを抑制するために、常温に戻さず60～150℃で素早く色素を吸着させるのが好ましい。また、凝集のような色素同士の相互作用を低減する目的で、無色の化合物を半導体微粒子に共吸着させてもよい。共吸着させる化合物としては界面活性化合物が有効であり、カルボキシル基を有するステロイド化合物（例えばケノデオキシコール酸）や以下に示すスルホン酸塩類等の界面活性化合物が使用できる。

【０１２６】

【化38】

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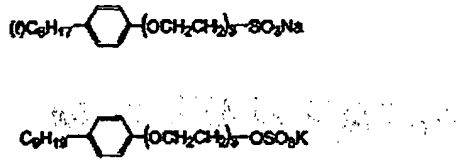

【０１２７】未吸着の色素は吸着後速やかに洗浄により除去するのが好ましい。洗浄は湿式洗浄槽中で．アセトニトリル等の極性溶剤やアルコール系溶剤等の有機溶媒を用いて行うのが好ましい。余分な色素の除去を促進する目的で、色素を吸着した後にアミン類や４級アンモニウム塩を用いて半導体微粒子の表面を処理してもよい。好ましいアミン類としてはピリジン．4-t-ブチルピリジン．ポリビニルピリジン等が挙げられる。好ましい４級アンモニウム塩としてはテトロブチルアンモニウムヨージド．テトラヘキシルアンモニウムヨージド等が挙げられる。これらは．有機溶媒に溶解して用いてもよく、液体の場合はそのまま用いてもよい。

【０１２８】(C)電荷輸送層

電荷輸送層は色素の酸化体に電子を補充する機能を有する。電荷輸送層に上記本発明の第一の電解質組成物又は第二の電解質組成物を用いるが、更に固体電解質や正孔（ホール）輸送材料を併用してもよい。

【０１２９】電荷輸送層はキャスト法．塗布法．浸漬法．含浸法、浸透法等により電極上に反応溶液層を形成し．次いで上記重合反応を行い設置することができる。加熱して重合させる場合．加熱温度は使用する色素の耐熱温度に応じて選択すればよいが、好ましくは10～200℃．より好ましくは30～150℃とする。加熱時間は加熱温度等にもよるが、５分～72時間程度とする。

【０１３０】電荷輸送層の形成方法に関して、詳しくは２通りの方法が可能である。１つは感光層の上に先に対極を貼り合わせておき、その間隙に上記反応溶液層を挟み込む方法である。もう１つは感光層上に直接電荷輸送層を形成し、その後対極を設置する方法である。前者の方法においては．浸漬等による毛管現象を利用する常圧プロセス、又は常圧より低い圧力にして間隙の気相を液相に置換する真空プロセスにより反応溶液層を挟み込むことができる。後者の方法においては．湿式電解質組成物を用いる場合は未乾燥のまま対極を付与しエッジ部に液漏洩防止措置を施せばよい。ゲル電解質を用いる場合は．液状の電解質組成物を塗布した後．固体化すればよい。また、湿式有機正孔輸送材料やゲル電解質を用いる場合は、前述の感光層の形成法と同様の方法を利用できる。

【０１３１】固体電解質や固体の正孔（ホール）輸送材料を用いる場合には、真空蒸着法やCVD法等のドライ成膜法により電荷輸送層を形成し、その後対極を付与することができる。有機正孔輸送材料は真空蒸着法．キャスト法．塗布法．スピンコート法、浸漬法、電解重合法、

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光電解重合法等の手法により導入することができる。無機固体化合物の場合も、キャスト法．塗布法、スピンコート法、浸漬法．電解析出法、無電解メッキ法等の手法により導入することができる。

【０１３２】酸化還元対を生成させるために電荷輸送層にヨウ素等を導入する場合．電解質の溶液に添加する方法．電荷輸送層の形成後．これをヨウ素等と共に密閉容器内に置き電解質中に拡散させる手法等が利用できる。また．後述の対極にヨウ素等を塗布又は蒸着し．光電変換素子を組み立てたときに電荷輸送層中に導入することも可能である。

【０１３３】電荷輸送層中の水分は10,000ppm以下であるのが好ましく．更に好ましくは2,000ppm以下であり、特に好ましくは100ppm以下である。

【０１３４】(D)対極

対極は光電変換素子を光電池としたときに正極として作用する。対極は上記導電性支持体と同様に、導電性材料からなる対極導電層のみから構成されていてもよいし、対極導電層と支持基板から構成されていてもよい。対極導電層に用いる導電性材料としては．金属（例えば白金．金、銀、銅．アルミニウム、マグネシウム．インジウム等）、炭素及び導電性金属酸化物（インジウムースズ複合酸化物．酸化スズにフッ素をドープしたもの等）が挙げられる。中でも白金．金、銀．銅、アルミニウム及びマグネシウムが好ましい。対極に用いる支持基板は．好ましくはガラス基板又はプラスチック基板であり．これに上記導電性材料を塗布又は蒸着して用いる。対極導電層の厚さは特に制限されないが３nm～10μmであるのが好ましい。対極の表面抵抗は低い程よく．50Ω/□以下であるのが好ましく、20Ω/□以下であるのがより好ましい。

【０１３５】導電性支持体と対極のいずれか一方又は両方から光を照射してよいので、感光層に光が到達するためには、導電性支持体と対極のうち少なくとも一方が実質的に透明であればよい。発電効率向上の観点からは、導電性支持体を透明にし．光を導電性支持体側から入射させるのが好ましい。この場合、対極は光を反射する性質を有するのが好ましい。このような対極の材料としては．金属や導電性の酸化物を蒸着したガラス又はプラスチック、金属薄膜等が使用できる。

【０１３６】対極は電荷輸送層上に直接導電材を塗布、メッキ又は蒸着（PVD．CVD）するか．導電層を有する基板の導電層側を貼り付けて設けてよい。また、導電性支持体の場合と同様に、特に対極が透明の場合には．対極の抵抗を下げる目的で金属リードを用いるのが好ましい。なお、好ましい金属リードの材質及び設置方法、金属リード設置による入射光量の低下等は導電性支持体の場合と同じである。

【０１３７】(E)その他の層

対極と導電性支持体の短絡を防止するため、予め導電性

支持体と感光層の間に緻密な半導体の薄膜層を下塗り層として塗設するのが好ましい。電荷輸送層に電子輸送材料や正孔輸送材料を用いる場合は特に有効である。下塗り層の材料は好ましくはTiO_2、SnO_2、Fe_2O_3、WO_3、ZnO及び／又はNb_2O_5であり、さらに好ましくはTiO_2である。下塗り層はElectrochim. Acta, 40, 643-652 (1995)に記載されているスプレーパイロリシス法や、スパッタ法等により塗設することができる。下塗り層の膜厚は5～1000nmであるのが好ましく、10～500nmであるのがより好ましい。

【０１３８】また、電極として作用する導電性支持体及び対極の一方又は両方の外側表面、導電層と基板の間又は基板の中間に、保護層、反射防止層等の機能性層を設けてもよい。このような機能性層の形成には、その材質に応じて塗布法、蒸着法、貼り付け法等を用いることができる。

【０１３９】(F)光電変換素子の内部構造の具体例

上述のように、光電変換素子の内部構造は目的に合わせ様々な形態が可能である。大きく２つに分ければ、両面から光の入射が可能な構造と、片面からのみ可能な構造が可能である。図２～図８に本発明に好ましく適用できる光電変換素子の内部構造を例示する。

【０１４０】図２に示す構造は、透明導電層10aと透明対極導電層40aとの間に、感光層20と電荷輸送層30とを介在させたものであり、両面から光が入射する構造である。図３に示す構造は、透明基板50a上に一部金属リード11を設け、その上に透明導電層10aを設け、下塗り層60、感光層20、電荷輸送層30及び対極導電層40をこの順で設け、更に支持基板50を配置したものであり、導電層側から光が入射する構造である。図４に示す構造は、支持基板50上に更に導電層10を設置し、下塗り層60を介して感光層20を設け、更に電荷輸送層30と透明対極導電層40aとを設け、一部に金属リード11を設けた透明基板50aを金属リード11側を内側にして配置したものであり、対極側から光が入射する構造である。図５に示す構造は、一部金属リード11を設けた２つの透明基板50a上に、それぞれ透明導電層10a、透明対極導電層40aを設け、それらの間に下塗り層60、感光層20及び電荷輸送層30を介在させたものであり、両面から光が入射する構造である。図６に示す構造は、透明基板50a上に透明導電層10aを設置し、下塗り層60を介して感光層20を設け、更に電荷輸送層30及び対極導電層40を設け、この上に支持基板50を配置したものであり、導電層側から光が入射する構造である。図７に示す構造は、支持基板50上に導電層10を設置し、下塗り層60を介して感光層20を設け、更に電荷輸送層30及び透明対極導電層40aを設け、この上に透明基板50aを配置したものであり、対極側から光が入射する構造である。図８に示す構造は、透明基板50a上に透明導電層10aを設置し、下塗り層60を介して感光層20を設け、更に電荷輸送層30及び透明対極導電層40aを設け、この上に透明基板50aを配置したものであり、両面から光が入射する構造である。

【０１４１】[3]光電池

本発明の光電池は、上記本発明の光電変換素子を外部負荷に接続して電気的仕事（発電）をさせるようにしたものである。光電池のうち、電荷輸送材料23が主としてイオン輸送材料からなるものを光電気化学電池と呼び、また太陽光による発電を主目的とするものを太陽電池と呼ぶ。

【０１４２】光電池の側面は構成物の劣化や内容物の揮散を防止するためにポリマーや接着剤等で密封するのが好ましい。導電性支持体及び対極にリードを介して接続される外部回路自体は公知のもので良い。

【０１４３】本発明の光電変換素子を太陽電池に適用する場合、そのセル内部の構造は基本的に上述した光電変換素子の構造と同じである。また、本発明の光電変換素子を含む本発明の太陽電池モジュールは、従来の太陽電池モジュールと基本的には同様の構造をとりうる。太陽電池モジュールは一般的には金属、セラミック等の支持基板の上にセルが構成され、その上を充填樹脂や保護ガラス等で覆い、支持基板の反対側から光を取り込む構造をとる。支持基板に強化ガラス等の透明材料を用い、その上にセルを構成してその透明の支持基板側から光を取り込む構造とすることも可能である。具体的には、スーパーストレートタイプ、サブストレートタイプ或いはポッティングタイプのモジュール構造、アモルファスシリコン太陽電池等で用いられる基板一体型モジュール構造等が知られている。本発明の光電変換素子を用いた色素増感型太陽電池においても、使用目的や使用場所及び環境により、適宜モジュール構造を選択できる。本発明における利用可能な太陽電池モジュールの構造、好ましい態様等は特願平11-8457に記載のものと同様である。

【０１４４】

【実施例】以下、具体例により本発明を更に詳細に説明するが、本発明はそれらに限定されるものではない。

【０１４５】１．二酸化チタン分散液の調製

内側をテフロン（登録商標）コーティングした内容積200mlのステンレス製容器に二酸化チタン微粒子（日本アエロジル（株）製、Degussa P-25）15g、水45g、分散剤（アルドリッチ社製、Triton X-100）1g、直径0.5mmのジルコニアビーズ（ニッカトー社製）30gを入れ、サンドグラインダーミル（アイメックス社製）を用いて1500rpmで２時間分散処理した。得られた分散液からジルコニアビーズをろ過により除去した。得られた分散液中の二酸化チタン微粒子の平均粒径は2.5μmであった。なお粒径はMALVERN社製のマスターサイザーにて測定した。

【０１４６】２．色素を吸着したTiO_2電極の作成

フッ素をドープした酸化スズ層を有する導電性ガラス（旭硝子（株）製TCOガラス-Uを20mm×20mmの大きさに切断加工したもの、表面抵抗約30Ω/□）の導電面側に

ガラス棒を用いて上記分散液を塗布した。半導体微粒子の塗布量は20g/m²とした。その際、導電面側の一部（端から3mm）に粘着テープを張ってスペーサーとし、粘着テープが両端に来るようにガラスを並べて一度に８枚ずつ塗布した。塗布後、粘着テープを剥離し、室温で１日間風乾した。次にこのガラスを電気炉（ヤマト科学（株）製マッフル炉FP-32型）に入れ、450℃にて30分間焼成し、TiO_2電極を得た。この電極を取り出し冷却した後、色素R-1のエタノール溶液（3×10^{-4}mol/l）に３時間浸漬した。色素の染着したTiO_2電極を4-t-ブチルピリジンに15分間浸漬した後、エタノールで洗浄し自然乾燥した。得られた感光層の厚さは6.5μmであった。

【０１４７】３．光電気化学電池の作製

3-1．溶媒を含有する電解質組成物を用いた光電気化学電池

実施例１～７並びに比較例１及び２

0.5mol/lの電解質塩MHIm（1-メチル-3-ヘキシルイミダゾリウムのヨウ素塩）及び0.05mol/lのヨウ素を含むアセトニトリル溶液を調製し、これにシロキサン化合物1-4を加えた。ここでシロキサン化合物は［溶媒＋電解質塩＋シロキサン化合物］を100質量％として10質量％用いた。得られた溶液を、前述のように作製した色素増感TiO_2電極基板（20mm×20mm）と、これと同じ大きさの白＊金蒸着ガラスを重ね合わせた隙間に毛細管現象を利用して染み込ませTiO_2電極中に導入し、エポキシ系封止剤で封止して、本発明の第一の電解質組成物を用いた実施例１の光電気化学電池を得た。溶媒及びシロキサン化合物を下記表１に示すように変更したこと以外は上記実施例１と同様にして、本発明の第一の電解質組成物を用いた実施例２～７の光電気化学電池を得た。また、シロキサン化合物を加えないこと以外は上記実施例１と同様にして比較例１の光電気化学電池を作製し、更にシロキサン化合物に換えてt-ブチルピリジンを添加したこと以外は上記実施例１と同様にして比較例２の光電気化学電池を作製した。上記実施例１～７並びに比較例１及び２の光電気化学電池に用いた色素、シロキサン化合物及びその質量比、電解質塩及びその濃度、ヨウ素の濃度、並びに溶媒を表１に併せて示す。なお、表１中のANはアセトニトリルを表し、NMOは3-メチル-2-オキサゾリジノンを表し、PCはプロピレンカーボネートを表し、MHImは1-メチル-3-ヘキシルイミダゾリウムのヨウ素塩を表す。また、表１中、シロキサン化合物の質量比は［溶媒＋電解質塩＋シロキサン化合物］を100質量％とした場合の質量比である。

【０１４８】

【表１】

光電気化学電池	色素	シロキサン化合物（質量%）	電解質塩（mol/l）	ヨウ素（mol/l）	溶媒
実施例1	R-1	1-4 (10)	MHIm (0.5)	0.05	AN
実施例2	R-1	1-4 (10)	MHIm (0.5)	0.05	NMO
実施例3	R-1	1-4 (10)	MHIm (0.5)	0.05	PC
実施例4	R-1	1-6 (10)	MHIm (0.5)	0.05	AN
実施例5	R-1	1-11 (10)	MHIm (0.5)	0.05	AN
実施例6	R-1	1-13 (10)	MHIm (0.5)	0.05	AN
実施例7	R-1	1-17 (10)	MHIm (0.5)	0.05	AN
比較例1	R-1	なし	MHIm (0.5)	0.05	AN
比較例2	R-1	t-ブチルピリジン (10)	MHIm (0.5)	0.05	AN

【０１４９】実施例８～17

0.5mol/lの電解質塩MHIm（1-メチル-3-ヘキシルイミダゾリウムのヨウ素塩）及び0.05mol/lのヨウ素を含むアセトニトリル溶液を調製した。この溶液にシロキサン化合物1-4を加え、更に求電子剤E-3を混合して均一な溶液を調整した。ここで、シロキサン化合物は［溶媒＋電解質塩＋シロキサン化合物］を100質量％として10質量％用い、求電子剤はシロキサン化合物の反応部位に対する求電子剤の求電子部位のモル比が１となるように加えた。得られた溶液を、前述のように作製した色素増感TiO_2電極基板（20mm×20mm）と、これと同じ大きさの白金蒸着ガラスを重ね合わせた隙間に毛細管現象を利用して染み込ませ、TiO_2電極中に導入した。これを50℃で12時間放置して室合反応を行い、エポキシ系封止剤で封止して、本発明の第二の電解質組成物を用いた実施例８の光電気化学電池を得た。溶媒、シロキサン化合物、並びに求電子剤とそのモル比を下記表２に示すように変更したこと以外は上記実施例８と同様にして、本発明の第二の電解質組成物を用いた実施例９～14の光電気化学電池を得た。また、シロキサン化合物を表２に示すものに換え、求電子剤の使用量をシロキサン化合物に対して５質量％としたこと以外は上記実施例８と同様にして、本発明の第二の電解質組成物を用いた実施例15～17の光電気化学電池を得た。上記実施例８～17の光電気化学電池に用いた色素、求電子剤及びそのモル比、シロキサン化合物及びその質量比、電解質塩及びその濃度、ヨウ素の濃度、並びに溶媒を表２に併せて示す。なお、表２中のANはアセトニトリルを表し、NMOは3-メチル-2-オキサゾリジノンを表し、PCはプロピレンカーボネートを表し、MHImは1-メチル-3-ヘキシルイミダゾリウムのヨウ素塩を表す。また、表２中、シロキサン化合物の質量比は［溶媒＋電解質塩＋シロキサン化合物］を100質量％とした場合の質量比であり、求電子剤のモル比は、シロキサン化合物の反応部位に対する求電子剤の求電子部位のモル比である。ただし、実施例15～17の光電気化学電池に用いた求電子剤の使用量はモル比ではなくシロキサン化合物に対する質量比（wt%）で示す。

【０１５０】

【表２】

光電気化学電池	色素	水電子剤（モル比又は質量比）	シロキサン化合物（質量%）	電解質塩（mol/l）	ヨウ素（mol/l）	溶媒
実施例8	R-1	E-3 (1)	1-4 (10)	MHIm (0.5)	0.05	AN
実施例9	R-1	E-3 (1)	1-4 (10)	MHIm (0.5)	0.05	NMO
実施例10	R-1	E-3 (1)	1-4 (10)	MHIm (0.5)	0.05	PC
実施例11	R-1	E-3 (1)	1-8 (10)	MHIm (0.5)	0.05	AN
実施例12	R-1	E-12 (1)	1-4 (10)	MHIm (0.5)	0.05	AN
実施例13	R-1	E-12 (1)	1-8 (10)	MHIm (0.5)	0.05	AN
実施例14	R-1	E-3 (0.9), E-5 (0.1)	1-4 (10)	MHIm (0.5)	0.05	AN
実施例15	R-1	E-3 (5 wt%)	1-11 (10)	MHIm (0.5)	0.05	AN
実施例16	R-1	E-3 (5 wt%)	1-13 (10)	MHIm (0.5)	0.05	AN
実施例17	R-1	E-3 (5 wt%)	1-17 (10)	MHIm (0.5)	0.05	AN

【０１５１】比較例３

500mgのヘキサエチレングリコールメタクリル酸エステル（日本油脂化学社製「ブレンマーPE-350」）．１gのプロピレンカーボネート．及び２mgの重合開始剤AIBNを含有する混合液を調製し．これに500mgのヨウ化リチウムを溶解させた。次にこの混合液を10分間真空脱気し、上記のように作製した色素増感TiO_2電極基板（20mm×20mm）に塗布した。続いて混合液を塗布したTiO_2電極を減圧下に置き、TiO_2電極内の気泡を除きモノマーの浸透を促した後、60℃で１時間加熱し重合させた。重合後、室温でヨウ素雰囲気下に30分間曝して．得られた重合体中にヨウ素を拡散させた。これを白金を蒸着した対極と重ね合せて比較例３の光電気化学電池（日本化学会誌，７、484頁（1997年）記載の電解質を用いた光電気化学電池）を得た。

【０１５２】3-2．室温溶融塩を含有する電解質組成物を用いた光電気化学電池

実施例18～28及び比較例４～６

60質量%の溶融塩A．28質量%の溶融塩B．２質量%のヨウ素．及び10質量%のシロキサン化合物1-4を混合し均一な電解質組成物を調製した。得られた電解質組成物５μlを上記のように作製した色素増感TiO_2電極基板に塗＊布した後、この電極を減圧下に置き電解質組成物を浸透させた。電解質組成物が十分に浸透し電極中の空気が抜けた後、これに白金蒸着ガラスを重ね合わせて本発明の第一の電解質組成物を用いた実施例18の光電気化学電池を得た。溶融塩とその質量比、並びにシロキサン化合物を下記表３に示すように変更したこと以外は上記実施例18と同様にして．本発明の第一の電解質組成物を用いた実施例19～28の光電気化学電池を得た．また、シロキサン化合物を加えず、溶融塩とその質量比を表３に示すように変更したこと以外は上記実施例18と同様にして比較例４及び５の光電気化学電池を作製し．更にシロキサン化合物に換えてt-ブチルピリジンを添加し、溶融塩とその質量比を表３に示すように変更したこと以外は上記実施例18と同様にして比較例６の光電気化学電池を作製した。ただし、t-ブチルピリジンの量は10質量%とした。上記実施例18～28及び比較例４～６の光電気化学電池に用いた色素、溶融塩及びその質量比．ヨウ素の質量比、並びにシロキサン化合物及びその質量比を表３に併せて示す。また、溶融塩A～Dの構造を以下に示す。

【０１５３】

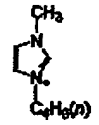
【表３】

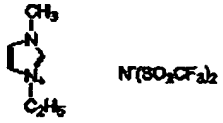
光電気化学電池	色素	溶融塩（質量%）	ヨウ素（質量%）	シロキサン化合物（質量%）
実施例18	R-1	A (60) / B (28)	2	1-4 (10)
実施例19	R-1	A (60) / C (28)	2	1-4 (10)
実施例20	R-1	A (60) / C (28)	2	1-4 (10)
実施例21	R-1	A (60) / B (28)	2	1-8 (10)
実施例22	R-1	D (60) / C (28)	2	1-4 (10)
実施例23	R-1	D (60) / C (28)	2	1-4 (10)
実施例24	R-1	D (60) / C (28)	2	1-8 (10)
実施例25	R-1	D (60) / C (28)	2	1-4 (10)
実施例26	R-1	A (60) / C (28)	2	1-11 (10)
実施例27	R-1	A (60) / C (28)	2	1-13 (10)
実施例28	R-1	A (60) / C (28)	2	1-17 (10)
比較例4	R-1	A (70) / C (28)	2	なし
比較例5	R-1	D (70) / C (28)	2	なし
比較例6	R-1	A (60) / C (28)	2	t-ブチルピリジン

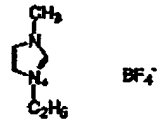
【０１５４】

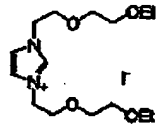
【化39】

55 56

A 

B 

C 

D 

【０１５５】実施例29～39

＊【表４】

光電気化学電池	色素	溶融塩（質量%）	ヨウ素（質量%）	求電子剤（モル比）	シロキサン化合物（質量%）
実施例29	R-1	A (60) / B (28)	2	E-3 (1)	1-4 (10)
実施例30	R-1	A (60) / C (28)	2	E-3 (1)	1-4 (10)
実施例31	R-1	A (60) / C (28)	2	E-12 (1)	1-4 (10)
実施例32	R-1	A (60) / B (28)	2	E-3 (1)	1-6 (10)
実施例33	R-1	D (60) / C (28)	2	E-3 (1)	1-4 (10)
実施例34	R-1	D (60) / C (28)	2	E-12 (1)	1-4 (10)
実施例35	R-1	D (60) / C (28)	2	E-3 (1)	1-6 (10)
実施例36	R-1	D (60) / C (28)	2	E-3 (0.9), E-5 (0.1)	1-4 (10)
実施例37	R-1	A (60) / C (28)	2	E-3 (1)	1-11 (10)
実施例38	R-1	A (60) / C (28)	2	E-3 (1)	1-13 (10)
実施例39	R-1	A (60) / C (28)	2	E-3 (1)	1-17 (10)

＊60質量%の溶融塩A、28質量%の溶融塩B、２質量%のヨウ素、及び10質量%のシロキサン化合物1-4を混合し、更に求電子剤E-3を加えて均一な電解質組成物を調製した。ここで、求電子剤は、シロキサン化合物の反応部位に対する求電子剤の求電子部位のモル比が１となるように加えた。得られた電解質組成物５μlを上記のように作製した色素増感TiO_2電極基板に塗布した後、この電極を減圧下に置き電解質組成物を浸透させた。電解質組成物が十分に浸透し電極中の空気が抜けた後、これに白金蒸着ガラスを重ね合わせ、50℃で10時間放置して重合反応を行い、本発明の第二の電解質組成物を用いた実施例29の光電気化学電池を得た。溶融塩及びシロキサン化合物とそれらの質量比、並びに求電子剤とそのモル比を下記表４に示すように変更したこと以外は上記実施例29と同様にして、本発明の第二の電解質組成物を用いた実施例30～39の光電気化学電池を得た。上記実施例29～39の光電気化学電池に用いた色素、溶融塩及びその質量比、ヨウ素の質量比、求電子剤及びそのモル比、並びにシロキサン化合物及びその質量比を表４に併せて示す。なお表４中、求電子剤のモル比は、シロキサン化合物の反応部位に対する求電子剤の求電子部位のモル比である。

【０１５６】

【０１５７】比較例７

プロピレンカーボネートに換えて上記化合物Cを用いたこと以外は上記比較例３と同様にして、比較例７の光電気化学電池を作製した。

【０１５８】４．光電変換効率の測定

500Wのキセノンランプ（ウシオ電気（株）製）の光をAM1.5フィルター（Oriel社製）及びシャープカットフィルター（Kenko L-42）を通すことにより紫外線を含まない模擬太陽光を発生させた。この光の強度は86mW/cm²であった。この模擬太陽光を、50℃にて作製した実施例１～39及び比較例１～７の光電気化学電池に照射し、発生した電気を電流電圧測定装置（ケースレーSMU238型）にて測定した。これにより求められた各光電気化学電池の短絡電流密度（Jsc）、開放電圧（Voc）、形状因子（FF）、変換効率（η）及び360時間連続照射後の変換効率の低下率を表５～８に示す。

【０１５９】

【表５】

光電気化学電池	短絡電流密度（Jsc） mA/cm²	開放電圧（Voc） V	形状因子（FF）	変換効率（η） %	η低下率（360時間後） %
実施例1	10.1	0.72	0.62	5.24	78
実施例2	9.75	0.72	0.61	4.98	76
実施例3	9.89	0.73	0.62	5.20	77
実施例4	10.2	0.72	0.61	5.21	76
実施例5	9.62	0.75	0.60	4.90	78
実施例6	9.43	0.74	0.61	4.95	78
実施例7	9.67	0.73	0.60	4.92	77
比較例1	9.92	0.65	0.63	4.87	99
比較例2	9.42	0.72	0.61	4.61	99

【０１６０】 ＊ ＊【表６】

光電気化学電池	短絡電流密度 (Jsc) mA/cm²	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (360時間後) %
実施例6	9.12	0.59	0.57	4.11	42
実施例9	8.97	0.67	0.56	3.84	35
実施例10	8.89	0.67	0.56	3.82	35
実施例11	9.10	0.66	0.57	3.85	41
実施例12	9.12	0.63	0.56	4.04	37
実施例13	9.10	0.59	0.56	3.81	33
実施例14	9.11	0.67	0.56	3.97	29
実施例15	7.87	0.65	0.56	3.40	33
実施例16	7.58	0.69	0.57	3.47	35
実施例17	7.90	0.68	0.57	3.95	37
比較例3	2.22	0.64	0.65	1.07	62

【０１６１】 ※ ※【表７】

光電気化学電池	短絡電流密度 (Jsc) mA/cm²	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (360時間後) %
実施例18	8.11	0.61	0.57	3.68	18
実施例19	8.08	0.62	0.58	3.80	18
実施例20	8.20	0.62	0.56	3.85	16
実施例21	8.11	0.60	0.56	3.69	17
実施例22	8.28	0.60	0.57	3.69	17
実施例23	8.14	0.60	0.58	3.76	16
実施例24	8.13	0.61	0.57	3.69	16
実施例25	8.09	0.61	0.58	3.74	14
実施例26	8.10	0.62	0.59	3.39	15
実施例27	8.98	0.60	0.57	3.58	16
実施例28	8.98	0.61	0.57	3.63	15
比較例4	7.85	0.62	0.58	2.76	35
比較例5	7.90	0.55	0.59	2.98	30
比較例6	7.20	0.62	0.58	2.91	45

【０１６２】 ★ ★【表８】

光電気化学電池	短絡電流密度 (Jsc) mA/cm²	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (360時間後) %
実施例29	8.11	0.57	0.55	2.96	18
実施例30	8.20	0.58	0.55	3.09	18
実施例31	8.20	0.59	0.54	3.09	16
実施例32	8.08	0.53	0.55	2.85	17
実施例33	8.28	0.60	0.55	3.18	17
実施例34	8.28	0.61	0.54	3.17	18
実施例35	8.26	0.58	0.55	3.06	18
実施例36	8.27	0.58	0.64	3.01	14
実施例37	8.01	0.60	0.55	2.84	16
実施例38	7.11	0.61	0.54	2.72	14
実施例39	7.05	0.60	0.54	2.68	16
比較例7	1.40	0.52	0.50	0.42	14

【０１６３】表５及び表７より明らかなように．比較例１．４及び５の光電気化学電池は開放電圧が低くこれが低い光電変換効率の原因となっているのに対して．本発明の第一の電解質組成物を用いた実施例１～７及び18～28の光電気化学電池は開放電圧が高くそれに伴い変換効率が向上している。また．電解質組成物に有機溶媒を多く含む比較例１及び２並びに実施例１～７の光電気化学電池では暗所保存後の劣化が著しいが．本発明の第一の電解質組成物を用いることにより耐久性が改善されていることがわかる。また表６及び表８より．従来の固体電解質を用いた比較例３及び７の光電気化学電池と比較して．本発明の第二の電解質組成物を用いた実施例８～17及び29～39の光電気化学電池は優れた変換効率及び耐久性を示すことがわかる。

【０１６４】

【発明の効果】以上詳述したように．本発明の第一及び第二の電解質組成物は耐久性及び電荷輸送能に優れており．この電解質組成物を用いた光電変換素子及び光電池は優れた耐久性及び光電変換特性を示す。かかる光電池は太陽電池として極めて有効である。

【図面の簡単な説明】

【図１】 本発明の好ましい光電変換素子の構造を示す部分断面図である。

【図２】 本発明の好ましい光電変換素子の構造を示す部分断面図である。

【図３】 本発明の好ましい光電変換素子の構造を示す

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59　　60

部分断面図である。

【図４】　本発明の好ましい光電変換素子の構造を示す部分断面図である。

【図５】　本発明の好ましい光電変換素子の構造を示す部分断面図である。

【図６】　本発明の好ましい光電変換素子の構造を示す部分断面図である。

【図７】　本発明の好ましい光電変換素子の構造を示す部分断面図である。

【図８】　本発明の好ましい光電変換素子の構造を示す部分断面図である。

【符号の説明】

10・・・導電層

＊10a・・・透明導電層

11・・・金属リード

20・・・感光層

21・・・半導体微粒子

22・・・色素

23・・・電荷輸送材料

30・・・電荷輸送層

40・・・対極導電層

40a・・・透明対極導電層

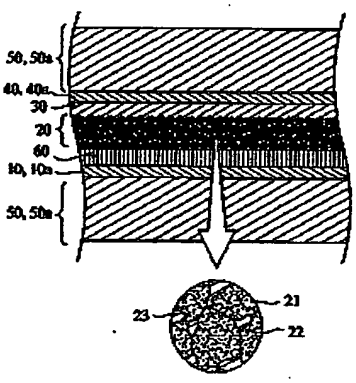
50・・・基板

50a・・・透明基板

60・・・下塗り層

＊

【図１】



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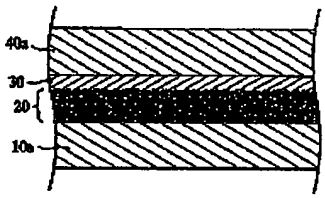
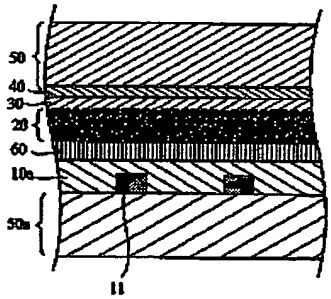
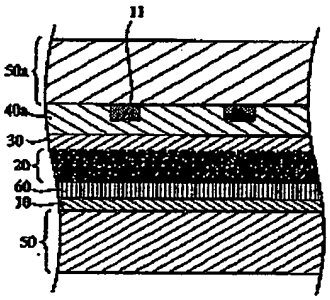


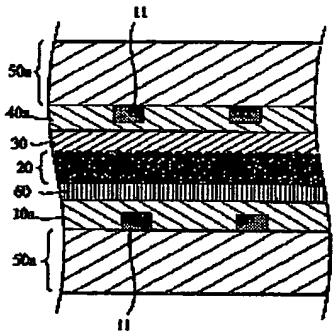
【図３】



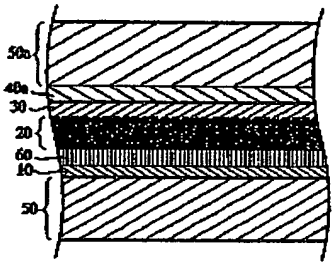
【図４】



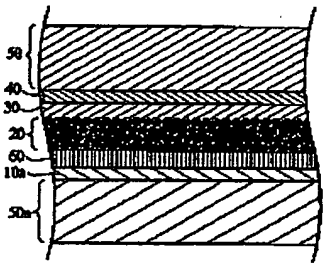
【図５】



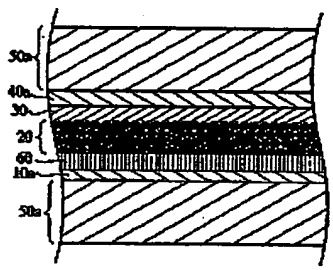
【図７】



【図6】



【図8】



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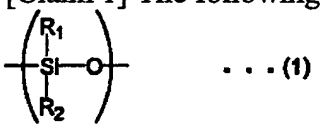
5F051 AA14 BA18 EA18 FA01 FA02 KA10
5G301 CA30 CD01
5H032 AA06 AS16 CC17 EE04 HH01 HH02

* NOTICES *

1. This document has been translated by computer.So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

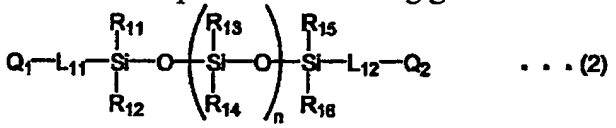
[Claim(s)]
[Claim 1] The following general formula (1) :. [Formula 1]



. . . (1)

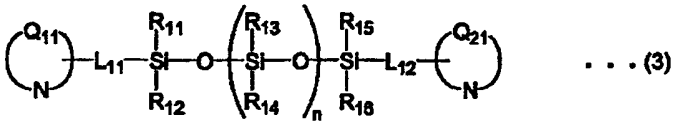
R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

(However, R1 L1- Q01 (L1 expresses combination or a divalent connection machine)) when Q01 expresses a substituent when L1 expresses combination, and L1 expresses a divalent connection machine, Q01 expresses a hydrogen atom or a substituent Expressing, R2 is L2-Q02 (when Q02 expresses a substituent when L2 expresses combination or a divalent connection machine and L2 expresses combination, and L2 expresses a divalent connection machine, Q02 exprésses a hydrogen atom or a substituent.). it expresses The electrolyte constituent characterized by containing the siloxane compound which has at least two substituents which react with an electrophile agent and can form covalent bond including the repeat unit expressed.
[Claim 2] The electrolyte constituent characterized by the substituent which reacts with the aforementioned electrophilic agent and can form covalent bond in an electrolyte constituent according to claim 1 being a basic group.
[Claim 3] The electrolyte constituent characterized by pKa(s) of the conjugate acid of the compound which comes to add hydrogen to the aforementioned basic group being 3-15 in an electrolyte constituent according to claim 2.
[Claim 4] The electrolyte constituent characterized by the aforementioned basic group being an imidazolyl machine which is not replaced [the pyridyl machine which is not replaced / substitution or /, substitution, or] in an electrolyte constituent according to claim 2 or 3.
[Claim 5] It sets to an electrolyte constituent according to claim 1 to 4, and the aforementioned siloxane compound is following general formula (2):. [Formula 2]



. . . (2)

(however the substituent which Q1 and Q2 react with the aforementioned electrophile agent independently, respectively, and can form covalent bond are expressed, R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], respectively, L11 and L12 express a divalent connection machine independently, respectively, and n expresses the integer of 1-1000. Electrolyte constituent characterized by what is expressed by).
[Claim 6] It sets to an electrolyte constituent according to claim 5, and the aforementioned siloxane compound is following general formula (3):. [Formula 3]



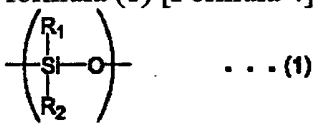
. . . (3)

(however Q11 and Q21 express the atomic group which forms 5 or 6 member ring with a nitrogen atom independently, respectively, R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], respectively, L11 and L12 express a divalent connection machine independently, respectively, and n expresses the integer of 1-1000. Electrolyte constituent characterized by what is expressed by).

[Claim 7] The electrolyte constituent characterized by being constituted with one or more sorts of atoms chosen from the group which the above Q11 and Q21 becomes from a carbon atom, a hydrogen atom, a nitrogen atom, an oxygen atom, and a sulfur atom, respectively in an electrolyte constituent according to claim 6.

[Claim 8] The electrolyte constituent characterized by the above 5 or 6 member rings being an imidazole ring or a pyridine ring in an electrolyte constituent according to claim 6 or 7.

[Claim 9] : The electrophile agent which has at least two leaving groups, and the following general formula (1) [Formula 4]

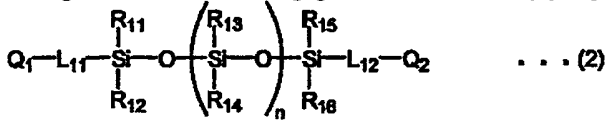


. . . (1)

R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

(However, R1 L1- Q01 (L1 expresses combination or a divalent connection machine)) when Q01 expresses a substituent when L1 expresses combination, and L1 expresses a divalent connection machine, Q01 expresses a hydrogen atom or a substituent Expressing, R2 is L2-Q02 (when Q02 expresses a substituent when L2 expresses combination or a divalent connection machine and L2 expresses combination, and L2 expresses a divalent connection machine, Q02 expresses a hydrogen atom or a substituent.). it expresses The electrolyte constituent characterized by containing the polymer which the siloxane compound which has at least two substituents which react with the aforementioned electrophile agent and can form covalent bond is made to react including the repeat unit expressed, and is obtained.

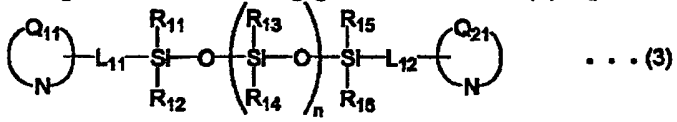
[Claim 10] It sets to an electrolyte constituent according to claim 9, and the aforementioned siloxane compound is following general formula (2):. [Formula 5]



. . . (2)

(however the substituent which Q1 and Q2 react with the aforementioned electrophile agent independently, respectively, and can form covalent bond are expressed, R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], respectively, L11 and L12 express a divalent connection machine independently, respectively, and n expresses the integer of 1-1000. Electrolyte constituent characterized by what is expressed by).

[Claim 11] It sets to an electrolyte constituent according to claim 10, and the aforementioned siloxane compound is following general formula (3):. [Formula 6]



. . . (3)

(however Q11 and Q21 express the atomic group which forms 5 or 6 member ring with a nitrogen

atom independently, respectively, R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], respectively, L11 and L12 express a divalent connection machine independently, respectively, and n expresses the integer of 1-1000. Electrolyte constituent characterized by what is expressed by).

[Claim 12] The electrolyte constituent characterized by pKa of the conjugate acid of the anion which the aforementioned leaving group ****s and produces in an electrolyte constituent according to claim 9 to 11 being ten or less.

[Claim 13] The electrolyte constituent characterized by the aforementioned leaving group being a halogen atom, an alkylsulfonyloxy machine, or an arylsulfonyloxy machine, respectively in an electrolyte constituent according to claim 9 to 12.

[Claim 14] The electrolyte constituent characterized by a solvent content being below 10 mass % of the whole electrolyte constituent in an electrolyte constituent according to claim 1 to 13.

[Claim 15] The electrolyte constituent characterized by containing an iodine salt and/or iodine in addition to the aforementioned siloxane compound and the aforementioned polymer in an electrolyte constituent according to claim 1 to 14.

[Claim 16] The electrolyte constituent characterized by being used for a photoelectric cell in an electrolyte constituent according to claim 1 to 15.

[Claim 17] The optoelectric transducer characterized by the aforementioned charge transporting bed containing an electrolyte constituent according to claim 1 to 16 in the optoelectric transducer which has a conductive layer, a photosensitive layer, a charge transporting bed, and a counter electrode.

[Claim 18] The optoelectric transducer characterized by containing the semiconductor particle to which sensitization of the aforementioned photosensitive layer was carried out with coloring matter in an optoelectric transducer according to claim 17.

[Claim 19] The optoelectric transducer characterized by the aforementioned semiconductor particle containing a metal chalcogenide particle in an optoelectric transducer according to claim 18.

[Claim 20] The optoelectric transducer characterized by the aforementioned metal chalcogenide particle containing a titanium oxide particle in an optoelectric transducer according to claim 19.

[Claim 21] The optoelectric transducer characterized by the aforementioned coloring matter being metal complex coloring matter and/or poly methine coloring matter in an optoelectric transducer according to claim 17 to 20.

[Claim 22] The photoelectric cell using the optoelectric transducer according to claim 17 to 21.

[Translation done.]

* NOTICES *

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2.**** shows the word which can not be translated.
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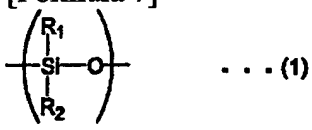
DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the optoelectric transducer and photoelectric cell in which the endurance and the photoelectric transfer characteristic which were excellent since the electrolyte constituent excellent in endurance and charge transportation ability and this electrolyte constituent were used are shown.
[0002]
[Description of the Prior Art] The liquefied electrolyte constituent (electrolytic solution) which dissolved the electrolyte salt in the solvent has been used from the former as an electrolyte of electrochemical elements, such as a cell, a capacitor, a sensor, a display device, and a record element. However, in the electrochemical element using such a liquefied electrolyte constituent, this constituent may be revealed between prolonged use or preservation, and reliability is missing.
[0003] Although U.S. JP,4927721,B etc. is indicating the optoelectric transducer using the semiconductor particle which carried out sensitization with coloring matter, and the photoelectrochemical cell using this in Nature, the 353rd volume, the 737-740th page, and 1991, since the liquefied electrolyte constituent is used for the charge transporting bed also in these, this constituent reveals or is drained between prolonged use or preservation, a photoelectric conversion efficiency falls remarkably or there is a case where it stops functioning as an element.
[0004] WO 93/No. 20565 proposed the optoelectric transducer which used the solid electrolyte under such a situation. Moreover, the Chemical Society of Japan, 7, 484 pages (1997) JP,7-288142,A, Solid State Ionics, 89, 263, and (1986) JP,9-27352,A proposed the optoelectric transducer containing the solid electrolyte which used the bridge formation polyethylene-oxide system high molecular compound. However, the optoelectric transducer using these solid electrolytes has the photoelectric transfer characteristic, especially inadequate short-circuit current density, and, in addition, its endurance is not enough, either.
[0005] Moreover, in order to prevent disclosure and an exhaustion of an electrolyte constituent and to raise the endurance of an optoelectric transducer, the method of using a pyridinium salt, an imidazolium salt, a thoria ZORIUMU salt, etc. is indicated (WO 95/No. 18456, JP,8-259543,A, electrochemistry, the 65th volume, No. 11, 923page (1997), etc.). These salts are in a melting state in ordinary temperature (near 25 degree C), and are called room temperature fused salt. Since solvents, such as water and an organic solvent, are unnecessary or little and can be managed with this method, the endurance of a cell improves. However, especially the optoelectric transducer using such room temperature fused salt has a low open circuit voltage, and its photoelectric conversion efficiency is not good.
[0006]
[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the optoelectric transducer and photoelectric cell in which the endurance and the photoelectric transfer characteristic which were excellent since the electrolyte constituent excellent in endurance and charge transportation ability and this electrolyte constituent were used are shown.
[0007]
[Means for Solving the Problem] The electrolyte constituent containing the polymer which this invention person makes the electrolyte constituent containing a siloxane compound including a

specific repeat unit and this siloxane compound react with an electrophilic agent wholeheartedly in view of the above-mentioned purpose as a result of research, and is obtained discovered that the outstanding charge transportation ability and outstanding endurance were shown, and hit on an idea of it to this invention.

[0008] namely, the first electrolyte constituent of this invention -- following general formula (1): --

[Formula 7]



. . . (1)

R_1: L_1-Q_{01}

R_2: L_2-Q_{02}

(However, R1 L1- Q01 (L1 expresses combination or a divalent connection machine)) when Q01 expresses a substituent when L1 expresses combination, and L1 expresses a divalent connection machine, Q01 expresses a hydrogen atom or a substituent Expressing, R2 is L2-Q02 (when Q02 expresses a substituent when L2 expresses combination or a divalent connection machine and L2 expresses combination, and L2 expresses a divalent connection machine, Q02 expresses a hydrogen atom or a substituent.). it expresses It is characterized by containing the siloxane compound which has at least two substituents which react with an electrophilic agent and can form covalent bond including the repeat unit expressed.

[0009] Moreover, it is characterized by the second electrolyte constituent of this invention containing the polymer which the siloxane compound which has the electrophilic agent which has at least two leaving groups, and at least two substituents which react with an electrophilic agent and can form covalent bond including the repeat unit expressed by the above-mentioned general formula (1) is made to react, and is obtained.

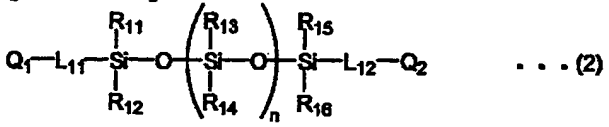
[0010] The first of this invention and second electrolyte constituents can be preferably used for a photoelectric cell. The optoelectric transducer of this invention has a conductive layer, a photosensitive layer, a charge transporting bed, and a counter electrode, and it is characterized by this charge transporting bed containing the electrolyte constituent of the above first, or the second electrolyte constituent. The photoelectric cell of this invention uses this optoelectric transducer.

[0011] By filling the following conditions with this invention, the optoelectric transducer and photoelectric cell in which the electrolyte constituent which has further excellent endurance or charge transportation ability, the further excellent endurance, and the photoelectric transfer characteristic are shown are obtained.

[0012] (1) In the first and second electrolyte constituents, as for the substituent which reacts with an electrophilic agent and can form covalent bond, it is desirable that it is a basic group, and this basic group is an imidazolyl machine which is not replaced [the pyridyl machine which is not replaced / substitution or /, substitution, or] especially preferably. As for pKa of the conjugate acid of the compound which comes to add hydrogen to this basic group, it is desirable that it is 3-15.

[0013] (2) As for the siloxane compound used for the first and second electrolyte constituents, being expressed by the following general formula (2) is desirable, and being expressed by the following general formula (3) is more desirable.

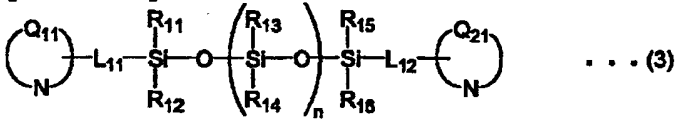
[Formula 8]



. . . (2)

The substituent which Q1 and Q2 react with the above-mentioned electrophilic agent independently, respectively, and can form covalent bond is expressed among a general formula (2), R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], respectively, L11 and L12 express a divalent connection machine independently, respectively, and n expresses the integer of 1-1000.

[Formula 9]



. . . (3)

Q11 and Q21 express the atomic group which forms 5 or 6 member ring with a nitrogen atom independently, respectively among a general formula (3), R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], respectively, L11 and L12 express a divalent connection machine independently, respectively, and n expresses the integer of 1-1000.

[0014] (3) As for Q11 and Q21 in a general formula (3), in the first and second electrolyte constituents, it is desirable respectively to be constituted by one or more sorts of atoms chosen from the group which consists of a carbon atom, a hydrogen atom, a nitrogen atom, an oxygen atom, and a sulfur atom.

[0015] (4) As for 5 or 6 member ring which Q11 and Q21 in a general formula (3) form with a nitrogen atom, respectively, in the first and second electrolyte constituents, it is desirable that they are especially an imidazole ring or a pyridine ring.

[0016] (5) As for pKa of the conjugate acid of the anion which the leaving group which an electrophilic agent has ****s and produces, in the second electrolyte constituent, it is desirable that it is ten or less.

[0017] (6) As for the leaving group which an electrophilic agent has, in the second electrolyte constituent, it is desirable respectively that they are a halogen atom, an alkylsulfonyloxy machine, or an arylsulfonyloxy machine.

[0018] (7) As for the first and second solvent contents of an electrolyte constituent, it is desirable that it is especially below 10 mass % of the whole electrolyte constituent.

[0019] (8) As for the first and second electrolyte constituents, it is desirable to contain an iodine salt and/or iodine in addition to the above-mentioned siloxane compound and the above-mentioned polymer.

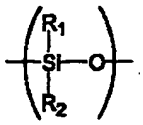
[0020] (9) As for the photosensitive layer of an optoelectric transducer, it is desirable to contain the semiconductor particle by which sensitization was carried out with coloring matter. As for this semiconductor particle, it is desirable that a metal chalcogenide particle is included, and, as for a metal chalcogenide particle, it is desirable that a titanium oxide particle is included. Moreover, as for coloring matter, it is desirable that they are metal complex coloring matter and/or poly methine coloring matter.

[0021]

[Embodiments of the Invention] [1] The first electrolyte constituent of an electrolyte constituent this invention contains the specific siloxane compound mentioned later. Moreover, the second electrolyte constituent of this invention contains the polymer which this siloxane compound is made to react with the electrophile agent which has at least two leaving groups, and is obtained. The second electrolyte constituent of this invention hardly shows a fluidity, but is excellent in endurance and charge transportation ability. The first of this invention and second electrolyte constituents may contain an electrolyte salt, a solvent, etc. further. Hereafter, each the first of this invention and second components of an electrolyte constituent are explained in full detail.

[0022] (A) The siloxane compound used for the first of a siloxane compound this invention and second electrolyte constituents has at least two substituents which react with an electrophile agent and can form covalent bond, including the repeat unit expressed by the following general formula (1). In the second electrolyte constituent of this invention, this siloxane compound receives ornamentation of alkylation, class[the / 4th]-izing, etc. by the electrophile agent.

[Formula 10]



. . . (1)

R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

[0023] R1 expresses L1-Q01 among a general formula (1), and R2 expresses L2-Q02. Here, when Q01 expresses a substituent when L1 expresses combination or a divalent connection machine and L1 expresses combination, and L1 expresses a divalent connection machine, Q01 expresses a hydrogen atom or a substituent. Moreover, when Q02 expresses a substituent when L2 expresses combination or a divalent connection machine and L2 expresses combination, and L2 expresses a divalent connection machine, Q02 expresses a hydrogen atom or a substituent. when they may also be included although a siloxane compound includes one repeat unit expressed by the general formula (1), and more than one are included, even if R1 and R2 in each repeat unit are the same respectively, they may differ [two or more]

[0024] When L1 or L2 expresses a divalent connection machine, as the example An alkylene machine, An alkenylene group, an arylene machine, -O-, -S-, -CO-, -NR'- (R' is a hydrogen atom or an alkyl group), - SO2- and - SiR" -- R'"- (R -- "and R'" -- Respectively -- Alkyl Group --) An aryl group, an alkoxy group or aryloxy groups, such combination, etc. are mentioned. Especially -(CH2) m1-, -O-, -(OCH2CH2) m1-, - M1-O-, -(OCH2CH2) M1-CH2-, (OCH2CH2) - M1-, -(OCH2CH2CH2) M1-O-, (OCH2CH</SUB>2CH2) - (OCH2CH2CH2) m1-CH2-, -(CH2) m1-(Si (CH3)2-O) m2-, and -O-(CH2) m1-(Si(CH3)2-O) m2- is desirable. In addition, m1 and m2 express the integer of 1-20, respectively.

[0025] the case where Q01 and Q02 express a substituent -- as the example of a desirable substituent -- an alkyl group (the shape of a straight chain --) You may be a letter of branching, or annular. For example, a methyl group, an ethyl group, n-propyl group, An isopropyl machine, t-butyl, n-octyl machine, a ray KOSHIRU machine, 2-chloro ethyl group, 2-cyano ethyl group, a 2-ethylhexyl machine, a cyclohexyl machine, a cyclopentylic group, aryl groups (for example, a phenyl group --), such as a 4-n-dodecyl cyclohexyl machine Heterocycle machines, such as p-tolyl group, a naphthyl group, and m-chlorophenyl machine (it is the univalent basis which comes preferably to remove one hydrogen atom from the aromatic heterocycle compound or un-aromatic heterocycle compound which is not replaced [the substitution of 5 or 6 members, or]) For example, 2-furil machine, 2-thienyl group, 2-pyrimidinyl group, 2-pyridyl machine, halogen atoms (for example, a chlorine atom --), such as 4-pyridyl machine and 1-imidazolyl machine a cyano group, a nitro group and hydroxyl groups, such as a bromine atom and an iodine atom, and an alkoxy group (for example, a methoxy machine --) An ethoxy basis, an isopropoxy group, a t-butoxy machine, n-octyloxy machine, a 2-methoxyethoxy machine, -O(CH2CH2O) mCH3 grade, and a silyloxy machine (for example, a trimethyl silyloxy machine --) t-buthyldimethyl silyloxy machine, a trimethoxy silyloxy machine, etc., an acyloxy machine (for example, a formyloxy machine, an acetyloxy machine, and a pivaloyloxy machine --) A stearoyl oxy-basis, a benzoyloxy machine, p-methoxypheny carbonyloxy group, etc., a carbamoyloxy machine (for example, N and an N-dimethylcarbamoyloxy machine --) A N,N-diethylcarbamoyloxy machine, morpholino carbonyloxy group, An N and N-G n-octyl aminocarbonyl oxy-basis, an N-n-octyl carbamoyloxy machine, etc., alkoxy carbonyloxy group (for example, a methoxycarbonyloxy machine --) An ethoxycarbonyloxy machine, t-buthoxycarbonyloxy machine, n-octyl carbonyloxy group, etc., aryloxy carbonyloxy group (for example, a phenoxy carbonyloxy machine --) p-methoxy phenoxy carbonyloxy machine, an p-n-hexadecyl oxy-phenoxy carbonyloxy machine, etc., the amino group (for example, the amino group, a methylamino machine, a dimethylamino machine, and the Ernie Reno machine --) the acylamino machines (for example, a formylamino machine --), such as N-methyl ANIRINO machine and a diphenylamino machine An acetylamino machine, the pivaloyl amino group, the lauroyl amino group, a benzoylamino machine, 3, 4, a 5-tree n-octyloxy phenyl carbonylamino machine, etc., the aminocarbonyl amino group (for example, carbamoyl amino machine, N, and N-dimethylamino carbonylamino machine --) N and N-

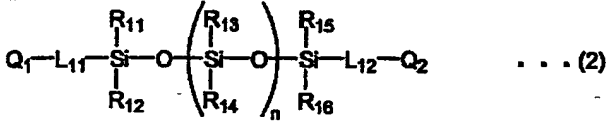
diethylamino carbonylamino machine, a morpholino carbonylamino machine, etc., an alkoxycarbonylamino machine (for example, a methoxycarbonylamino machine --) An ethoxycarbonylamino machine, t-butoxycarbonylamino machine, n-octadecyloxycarbonylamino machine, aryloxycarbonylamine machines (for example, a phenoxycarbonylamino machine --), such as N-methyl methoxycarbonylamino machine p-chloro phenoxycarbonylamino machine, an m-n-octyloxy phenoxycarbonylamino machine, etc., a sulfamoylamino group (for example, sulfamoylamino group, N, and N-dimethylamino sulfonylamino machine --) alkyl sulfonylamino machines (for example, a methylsulfonylamino machine --), such as an N-n-octyl amino sulfonylamino machine aryl sulfonylamino machines (for example, a phenyl sulfonylamino machine --), such as a butylsulphonylamino machine 2, 3, 5-TORIKURORO phenyl sulfonylamino machine, p-methylphenyl sulfonylamino machine, etc., a sulfhydryl group and an alkyl thio machine (for example, a methylthio machine and an ethyl thio machine --) aryl thio machines (for example, a phenylthio machine --), such as an n-hexadecyl thio machine heterocycle thio machines (for example, a 2-benzothiazolethio group --), such as p-chloro phenylthio machine and m-methoxy phenylthio machine sulfamoyl groups (for example, N-ethyl sulfamoyl group --), such as a 1-phenyl tetrazole-5-IRUCHIO machine N-(3-dodecyloxy propyl) sulfamoyl group, N, and N-dimethyl sulfamoyl group, N-acetyl sulfamoyl group, N-benzoyl sulfamoyl group, alkyl sulfinyl machines (for example, a methyl sulfinyl machine --), such as N-(N'-phenylcarbamoyl) sulfamoyl group aryl sulfinyl machines (for example, a phenyl sulfinyl machine --), such as an ethyl sulfinyl machine alkyl sulfonyl machines (for example, a methyl sulfonyl machine --), such as p-methylphenyl sulfinyl machine aryl sulfonyl machines (for example, a phenyl sulfonyl machine --), such as an ethyl sulfonyl machine acyl groups (for example, an acetyl group --), such as p-methylphenyl sulfonyl machine A pivaloyl machine, 2-chloro acetyl group, a stearoyl machine, a benzoyl, aryloxy carbonyl groups (for example, a phenoxy carbonyl group --), such as an p-n-octyloxy phenyl carbonyl group o-chloro phenoxy carbonyl group, m-nitroglycerine phenoxy carbonyl group, alkoxy carbonyl groups (for example, a methoxycarbonyl group --), such as a p-t-butyl phenoxy carbonyl group An ethoxycarbonyl machine, a t-butoxycarbonyl machine, n-octadecyl oxycarbonyl machine, etc., a carbamoyl group (for example, a carbamoyl group and N-methyl carbamoyl group --) An N and N-dimethyl carbamoyl-group, N, and N-G n-octyl carbamoyl group, Silyl machines, such as N-(methyl sulfonyl) carbamoyl group (it is the silyl machine which is not replaced [the substitution of carbon numbers 3-30, or] preferably) For example, a trimethylsilyl machine, t-butyldimethylsilyl machine, a phenyl dimethylsilyl machine, etc., Phosphino machines (being the phosphino machine which is not replaced [the substitution of carbon numbers 2-30 or] preferably for example, a dimethyl phosphino machine, a diphenyl phosphino machine, a methylphenoxy phosphino machine, etc.) etc. are mentioned. Especially, an alkyl group, an aryl group, a silyl machine, an alkoxy group, an aryloxy group, a silyloxy machine, a heterocycle machine, the amino group, an alkyl thio machine, and a phosphino machine are more desirable, and an alkyl group, a silyl machine, an alkoxy group, a silyloxy machine, and especially a heterocycle machine are desirable.

[0026] The above-mentioned siloxane compound has two or more substituents which react with an electrophile agent and can form covalent bond. As for the substituent which reacts with an electrophile agent and can form covalent bond, in the first and second electrolyte constituents, it is desirable that it is a basic group. pKa of the conjugate acid of the compound with which a basic group comes to add hydrogen to it points out three or more bases here. As for pKa of this conjugate acid, it is desirable that it is 3-15, and it is more desirable that it is 4-12. such a basic group -- the amino group (a dimethylamino machine and a diethylamino machine --) nitrogen-containing heterocycle machines (a morpholino machine and a quinuclidinyl machine --), such as the Ernie Reno machine A piperazinyl machine, a piperidino machine, a pyrrolidino machine, an imidazolyl machine, 2-methyl imidazolyl machine, A quinolyl machine, an acridinyl machine, a pyridyl machine, 2-methyl pyridyl machine, It is desirable that they are guanidino machines (trimethyl guanidino machine etc.), such as a diazabicyclo undecenyl machine, it is more desirable that it is a nitrogen-containing heterocycle machine, and it is desirable that it is especially the imidazolyl machine which is not replaced [the pyridyl machine which is not replaced / substitution or /, substitution, or]. The above-mentioned siloxane compound may have such a basic group at the side chain and/or end in the repeat unit

expressed by the general formula (1). When it has this basic group in the side chain in the repeat unit expressed by the general formula (1), Q01 in a general formula (1) and/or Q02 are these basic groups.

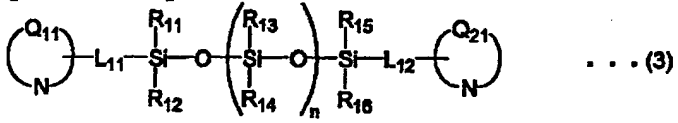
[0027] As for the siloxane compound used for the first of this invention, and second electrolyte constituents, being expressed by the following general formula (2) is desirable, and being expressed by the following general formula (3) is more desirable.

[Formula 11]



. . . (2)

[Formula 12]



. . . (3)

[0028] Q1 and Q2 express the substituent which reacts with an electrophile agent independently, respectively and can form covalent bond among a general formula (2). The electrophile agent in this substituent and the atom which reacts are a nitrogen atom, the Lynn atom, or a sulfur atom preferably, is a nitrogen atom or the Lynn atom more preferably, and is a nitrogen atom especially preferably. As a substituent which Q1 and Q2 express, the amino group, a phosphino machine, a heterocycle machine, an alkyl thio machine, etc. are mentioned.

[0029] R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or] among a general formula (2), respectively. R11-R16 are the alkyl groups of carbon numbers 1-10 preferably, are the alkyl group of carbon numbers 1-3 more preferably, and are a methyl group especially preferably.

[0030] The above Q1 and Q2, and R11-R16 may have the substituent, respectively. as the desirable example of this substituent -- an alkyl group (a methyl group and an ethyl group --) A propyl group, an isopropyl machine, a butyl, a pentyl machine, a hexyl machine, An octyl machine, a 2-ethylhexyl machine, t-octyl machine, a decyl group, the dodecyl, A tetradecyl machine, 2-hexyl decyl group, an octadecyl machine, a cyclohexyl machine, alkenyl machines (a vinyl group --), such as a cyclopentylic group, 2-carboxy ethyl group, and a benzyl A halogens atom, such as an allyl group (a fluorine atom, a chlorine atom, a bromine atom, iodine atom, etc.), A cyano group, an alkoxy group (a methoxy machine, an ethoxy basis, methoxyethoxy machine, etc.), aryloxy machines (phenoxy machine etc.) and an alkyl thio machine (a methylthio machine --) Acyl groups, such as an ethyl thio machine (an acetyl group, a propionyl machine, benzoyl, etc.), sulfonyl machines (a methane sulfonyl machine, benzenesulphonyl machine, etc.) and an acyloxy machine (an acetoxy machine --) sulfonyloxy machines (a methane sulfo NIRIOKISHI machine --), such as a benzoyloxy machine Phosphonyl groups, such as a toluenesulfonyloxy machine (diethyl phosphonyl group etc.), Amide groups (an acetylamino machine, benzoylamino machine, etc.), carbamoyl groups (N and N-dimethyl carbamoyl group, N-phenylcarbamoyl machine, etc.), an aryl group, heterocycle machines (a phenyl group, toluyl machine, etc.) (a pyridyl machine, an imidazolyl machine, furanyl machine, etc.), etc. are mentioned.

[0031] L11 and L12 express a divalent connection machine independently among a general formula (2), respectively. As an example of this divalent connection machine, the connection machine which comes to combine an alkylene machine, an alkenylene group, an arylene machine, -O-, -S-, -CO-, -NR'- (for R' to express a hydrogen atom or an alkyl group), -SO2-, -SiRR'- (for R and R' to express an alkyl group or an aryl group, respectively), and these [two / or more] is mentioned.

[0032] When L11 and L12 are an alkylene machine, an alkenylene group, or an arylene machine, These A halogen atom (a fluorine atom, a chlorine atom, a bromine atom, iodine atom, etc.), A hydroxyl group, the amino group, a nitro group, a carboxyl group, a carbamoyl group, a sulfonic group, A sulfonamide machine, acyl groups (a HORUMIRU machine, acetyl group, etc.), an acyloxy machine, The acylamino machine, alkyl groups (an acetamino machine, bends amino group, etc.),

You may have substituents, such as alkoxy groups (a methoxy machine, an ethoxy basis, methoxyethoxy machine, etc.), an AKOKISHI carbonyl group, an alkyl sulfonyl machine, an aryl group, an aryloxy group, and aryl sulfonyl machines (phenoxy machine etc.).

[0033] n expresses the integer of 1-1000 among a general formula (2). n is the integer of 1-500 preferably, and is the integer of 1-100 especially preferably. If n is larger than 1000, a reactant fall with ionic conductivity and an electrophile agent will be caused.

[0034] Q11 and Q21 express the atomic group which forms 5 or 6 member ring with a nitrogen atom independently, respectively among a general formula (3). As for Q11 and Q21, it is desirable to be constituted by one or more sorts of atoms chosen from the group which consists of a carbon atom, a hydrogen atom, a nitrogen atom, an oxygen atom, and a sulfur atom.

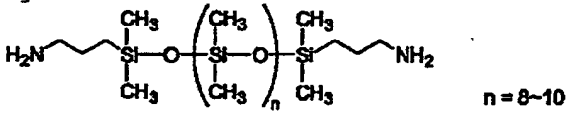
[0035] As for 5 or 6 member ring formed of Q11 and Q21, it is desirable that it is an unsaturation ring. As 5 member rings, a pyrrolidine ring, an oxazole ring, a thiazole ring, an imidazole ring, a pyrazole ring, an isoxazole ring, a thiadiazole ring, an oxadiazole ring, and a triazole ring are desirable, a thiazole ring, an imidazole ring, and a triazole ring are more desirable, and especially an imidazole ring is desirable. As 6 member rings, a morpholine ring, a piperidine ring, a pyridine ring, a pyrimidine ring, a pyridazine ring, a pyrazine ring, and a triazine ring are desirable, and especially a pyridine ring is desirable.

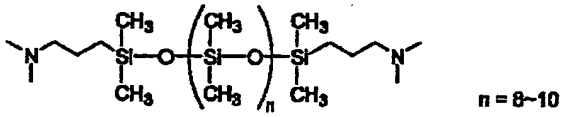
[0036] R11-R16, L11 and L12, and n in a general formula (3) are them in a general formula (2), and homonymy, and its same is said of a desirable mode.

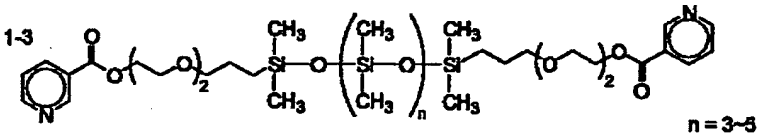
[0037] Although the example 1-1 to 1-18 of the siloxane compound used for the first of this invention and second electrolyte constituents is shown below, this invention is not limited to them.

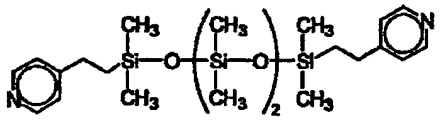
[0038]

[Formula 13]

1-1 

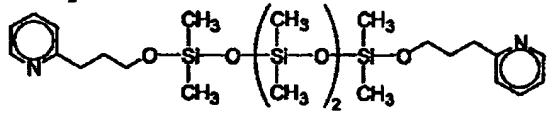
1-2 

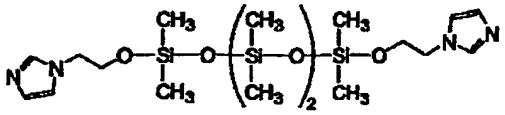
1-3 

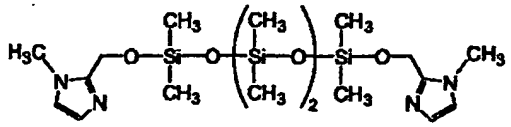
1-4 

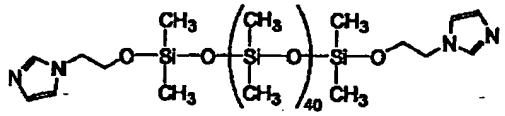
[0039]

[Formula 14]

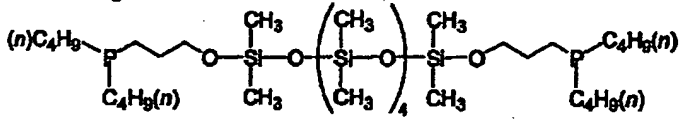
1-5 

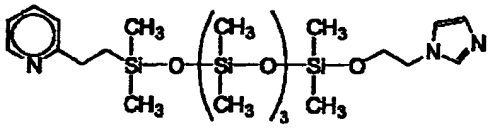
1-6 

1-7 

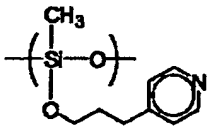
1-8 

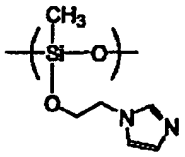
[0040]
[Formula 15]

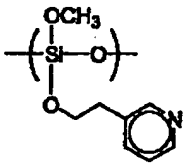
1-9 

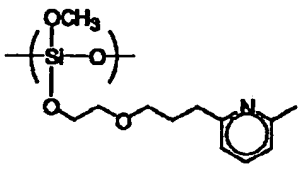
1-10 

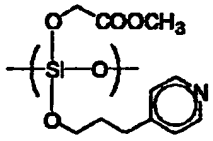
[0041]
[Formula 16]

1-11 

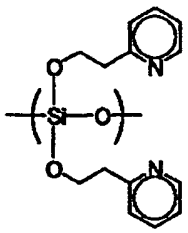
1-12 

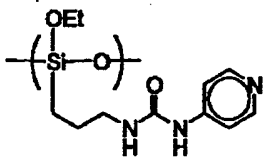
1-13 

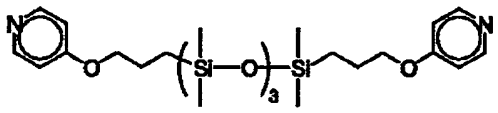
1-14 

1-15 

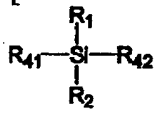
[0042]
[Formula 17]

1-16 

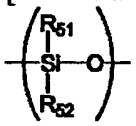
1-17 

1-18 

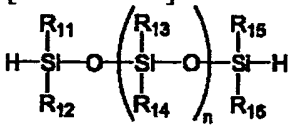
[0043] The siloxane compound used by this invention is easily compoundable with the substitution reaction by R1-H of a compound and/or R2-H which are expressed by the polymerization of the silane compound expressed by the following general formula (4), and the following general formula (5), the high DOROSHI relation reaction of the compound and olefin compound which are expressed by the following general formula (6), the condensation reaction of the compound and the alcoholic compound which are expressed by the following general formula (7), etc.
[0044]
[Formula 18]

 . . . (4)

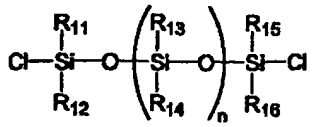
R41 and R42 express a halogen atom or an alkoxy group independently among a general formula (4), respectively.
[0045]
[Formula 19]

 . . . (5)

R51 and R52 express an alkoxy group or an aryloxy group independently among a general formula (5), respectively.
[0046]
[Formula 20]

 . . . (6)

R11-R16 and n in a general formula (6) are them in a general formula (2), and homonymy, and its same is said of a desirable mode.
[0047]
[Formula 21]



. . . (7)

R11-R16 and n in a general formula (7) are them in a general formula (2), and homonymy, and its same is said of a desirable mode.

[0048] (B) The electrophile agent used for the second electrolyte constituent of an electrophile agent this invention has at least two leaving groups. This electrophile agent reacts with "the substituent which reacts with an electrophile agent and can form covalent bond" which the above-mentioned siloxane compound has, and when alkylation, onium chlorination, the 4th class-ization, etc. carry out this substituent, it forms the shape of a straight line, and the polymer over which the bridge was constructed.

[0049] In order to make moderate the degree of cross linking of the polymer which the above-mentioned siloxane compound and an electrophile agent are made to react, and is obtained, as for the number of leaving groups, it is desirable that they are 2-4 pieces, and it is desirable that they are especially two pieces. If there are many leaving groups, a degree of cross linking will become high, consequently membraneous quality becomes hard, and ionic conductivity falls. Moreover, as for pKa of the conjugate acid of the anion which a leaving group ****s and produces, it is desirable that it is ten or less, and it is more desirable that it is five or less.

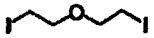
[0050] Leaving groups may be a halogen atom, an alkylsulfonyloxy machine, an arylsulfonyloxy machine, an acyloxy machine, etc., respectively. A halogen atom, an alkylsulfonyloxy machine, and an arylsulfonyloxy machine are desirable especially. As a halogen atom, an iodine atom, a bromine atom, and a chlorine atom are desirable, and an iodine atom and a bromine atom are more desirable. As an alkylsulfonyloxy machine, a methyl sulfonyloxy machine, a chloro methyl sulfonyloxy machine, and perfluoroalkyl sulfonyloxy machines (trifluoromethyl sulfonyloxy machine etc.) are desirable. As an arylsulfonyloxy machine, a benzene sulfonyloxy machine, a p-toluenesulfonyloxy machine, p-chlorobenzene sulfonyloxy machine, and p-nitrobenzene sulfonyloxy machine are desirable. As an acyloxy machine, the alkylcarbonyloxy machines (trifluoromethyl carbonyloxy group etc.) and aryl-carbonyloxy groups (p-fluoro phenyl carbonyloxy group etc.) which carried out fluorine substitution of all or a part of hydrogen atoms are desirable.

[0051] The amount of the electrophile agent used can be arbitrarily defined according to the molecular weight or the degree of cross linking of a reaction rate with the above-mentioned siloxane compound, or the polymer to generate. The 0.01-2Eq of the 0.05-1.5Eq of the amount of the electrophile agent used is 0.1-1Eq especially preferably more preferably preferably to the number of mols of "the substituent which reacts with an electrophile agent and can form covalent bond" which a siloxane compound has. When the number of mols of the substituent which reacts with the electrophile agent which a siloxane compound has, and can form covalent bond is not clear, the mass ratio of the electrophile agent to the mass of a siloxane compound is one to 100 mass % preferably, and is three to 70 mass % more preferably. Even if it uses an electrophile agent independently, it may use two or more sorts together. Although this invention shows the example E-1 to E-27 of an usable electrophile agent hereafter, this invention is not limited to them.

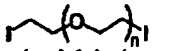
[0052]

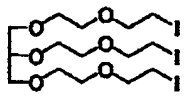
[Formula 22]

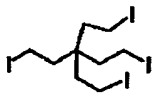
E-1 

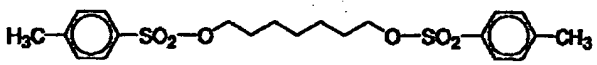
E-2 

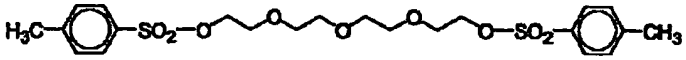
E-3 

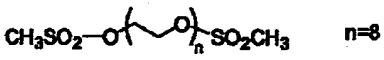
E-4  n=8

E-5 

E-6 

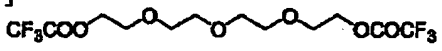
E-7 

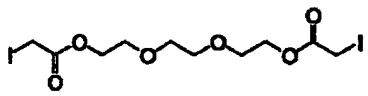
E-8 

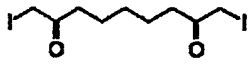
E-9 

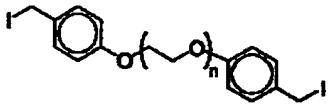
E-10 

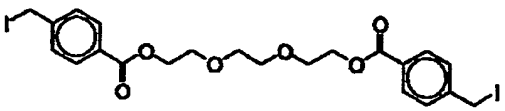
[0053]
[Formula 23]

E-11 

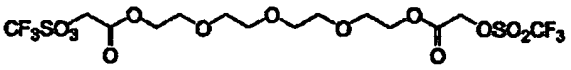
E-12 

E-13 

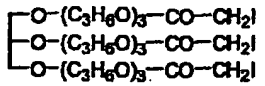
E-14 

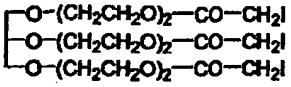
E-15 

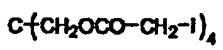
E-16 

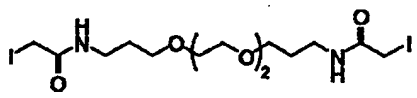
E-17 

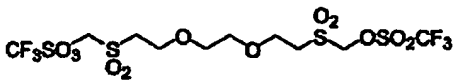
[0054]
[Formula 24]

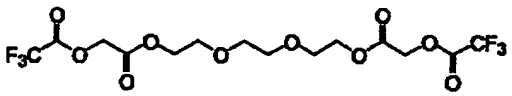
E-18 

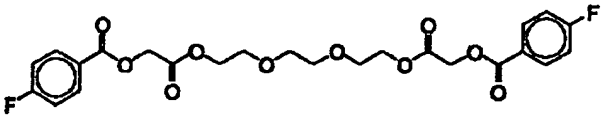
E-19 

E-20 

E-21 

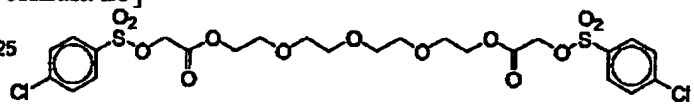
E-22 

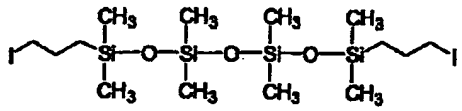
E-23 

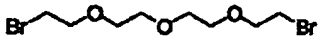
E-24 

[0055]

[Formula 25]

E-25 

E-26 

E-27 

[0056] (C) The polymer used for the second electrolyte constituent of a polymerization-reaction this invention can be obtained by the polymerization reaction of the above-mentioned electrophile agent and a siloxane compound. The polymerization of them is carried out by the alkylation reaction which occurs in detail between the electrophilic part in an electrophile agent, and the substituent which reacts with this electrophile agent in a siloxane compound, and can form covalent bond, the reaction (for example, the 4th class-ized reaction of nitrogen) which forms an onium salt. As for the mass average molecular weight of the polymer obtained, it is desirable that it is 1000-1 million, and it is more desirable that it is 2000-500,000.

[0057] As for polymerization reaction, it is desirable to carry out besides an electrophilic agent and a siloxane compound under the conditions with which the electrolyte salt mentioned later coexists. Although an electrolyte salt may be added after a reaction, it is difficult to distribute an electrolyte salt uniformly in a polymer in this case, and it is not desirable.

[0058] When preparing the reaction solution containing a siloxane compound, an electrophilic agent, and an electrolyte salt and performing polymerization reaction, when a [siloxane compound + electrolyte salt + solvent] is made into 100 mass %, as for the mass ratio of a siloxane compound, it is desirable to consider as 1 - 50 mass %, and it is more desirable to consider as 3 - 30 mass %. Since

carrier mobility will fall if a fluidity becomes that a siloxane compound is under 1 mass % inadequate and 60 mass % is exceeded, it is not desirable. In addition, even if it uses a siloxane compound independently, it may use two or more sorts together.

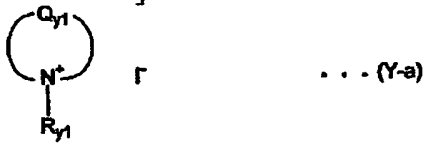
[0059] (D) As an electrolyte salt electrolyte salt, they are (a) I2 and an iodide (it LiI(s)), for example. NaI, KI, CsI, the metal iodide of CaI2 grade, tetrapod alkylammonium iodide, Combination with the 4th class ammonium iodine salts, such as pyridinium iodide and imidazolium iodide, etc., (b) -- Br2 and a bromide (LiBr, NaBr, KBr, CsBr, and the metal bromide of CaBr2 grade --) Combination with the 4th class ammonium bromine salts, such as a tetrapod alkylammonium star's picture and a pyridinium star's picture, etc., (c) Metal complexes (a ferrocyanic-acid salt-ferricyanic-acid salt, ferrocene-ferricinium ion, etc.), (d) sulfur compounds (the poly sodium sulfide, alkyl thiol-alkyl disulfide, etc.), (e) viologen coloring matter, a hydroquinone-quinone, etc. can be used. Especially, the combination of I2 and the 4th class ammonium iodine salt is desirable. You may mix and use an electrolyte salt.

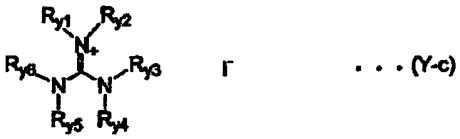
[0060] Moreover, EP718288, WO 95/18456, J.Electrochem.Soc., Vol.143, No.10, and 3099 (1996), as an electrolyte salt Inorg.Chem., 35, and 1168-1178 (1996), JP,8-259543,A, electrochemistry, the 65th volume, No. 11, and 923 pages (1997) etc. -- fused salt, such as a pyridinium salt indicated, an imidazolium salt, and a thoria ZORIUMU salt; can also be used The quality of molten salt electrolysis is desirable especially from a viewpoint of coexistence of endurance and charge transportation ability. In addition, fused salt here is liquefied in a room temperature, or it is the salt of the low melting point and it is [as for the melting point, it is desirable that it is 100 degrees C or less, and] desirable [the melting point] that it is especially near a room temperature.

[0061] as the fused salt which can be preferably used by this invention -- the following general formula (Y-a) -- what is expressed by either is mentioned for and (Y-b) (Y-c)

[0062]

[Formula 26]





[0063] Qy1 expresses the atomic group which forms the aromatic cation of 5 or 6 member ring with a nitrogen atom among a general formula (Y-a). As for Qy1, it is desirable to be constituted by one or more sorts of atoms chosen from the group which consists of a carbon atom, a hydrogen atom, a nitrogen atom, an oxygen atom, and a sulfur atom.

[0064] It is desirable that they are an oxazole ring, a thiazole ring, an imidazole ring, a pyrazole ring, an isoxazole ring, a thiadiazole ring, an oxadiazole ring, a triazole ring, the Indore ring, or a pyrrole ring, as for 5 member rings formed of Qy1, it is more desirable that they are an oxazole ring, a thiazole ring, or an imidazole ring, and it is desirable that they are especially an oxazole ring or an imidazole ring. As for 6 member rings formed of Qy1, it is desirable that they are a pyridine ring, a pyrimidine ring, a pyridazine ring, a pyrazine ring, or a triazine ring, and it is more desirable that it is a pyridine ring.

[0065] Ay1 expresses a nitrogen atom or the Lynn atom among a general formula (Y-b).

[0066] A general formula (Y-a), and (Y-b) (Y-c) inner Ry1-inner Ry6 are an alkyl group (even if it has the shape of the carbon atomic numbers 1-24 and a straight chain preferably and is a letter of branching) which is not replaced [substitution or] independently, respectively. You may be a ring type. Moreover, for example, a methyl group, an ethyl group, a propyl group, An isopropyl machine, a pentyl machine, a hexyl machine, an octyl machine, a 2-ethylhexyl machine, t-octyl machine, a decyl group, a dodecyl machine, a tetradecyl machine, 2-hexyl decyl group, ARUKENIRU machines which are not replaced [substitution or], such as an octadecyl machine, a cyclohexyl machine, and a cyclopentylic group (even if it has the shape of the carbon atomic numbers 2-24 and a straight chain preferably, you may be a letter of branching) For example, a vinyl group, an allyl group, etc. are expressed, and it is the alkyl group of the carbon atomic numbers 2-18, or the ARUKENIRU machine of the carbon atomic numbers 2-18 more preferably, and is the alkyl group of the carbon atomic numbers 2-6 especially preferably.

[0067] Moreover, among Ry1-Ry4 in a general formula (Y-b), the un-aromatic ring in which two or more connect with mutually and they contain Ay1 may be formed, two or more may connect mutually and they may form a ring structure among Ry1-Ry6 in a general formula (Y-c).

[0068] A general formula (Y-a), inner Qy1, and Ry1-Ry6 may have the substituent. as the desirable example of this substituent -- a halogen atom (it Cl(s) and Br(s) F --) cyano groups, such as I, and an alkoxy group (a methoxy machine, an ethoxy basis, and a methoxyethoxy machine --) Aryloxy machines (phenoxy machine etc.), such as a methoxyethoxy ethoxy basis, Alkyl thio machines (a methylthio machine, ethyl thio machine, etc.), an alkoxy carbonyl group (ethoxycarbonyl machine etc.), carbonate machines (ethoxycarbonyloxy machine etc.) and an acyl group (an acetyl group --) sulfonyl machines (a methane sulfonyl machine --), such as a propionyl machine and a benzoyl Acyloxy machines (an acetoxy machine, benzoyloxy machine, etc.), such as a benzenesulphonyl machine, A sulfonyloxy machine (a methane sulfonyloxy machine, toluenesulfonyloxy machine, etc.), phosphonyl groups (diethyl phosphonyl group etc.) and an amide group (an acetylamino machine --) Carbamoyl groups, such as a benzoylamino machine (N and N-dimethyl carbamoyl group etc.), an alkyl group (a methyl group, an ethyl group, a propyl group, an isopropyl machine, and a cyclo propyl group --) Aryl groups, such as a butyl, 2-carboxy ethyl group, and a benzyl, heterocycle machines (a phenyl group, toluyl machine, etc.) (a pyridyl machine, an imidazolyl machine, furanyl machine, etc.), ARUKENIRU machines (a vinyl group, 1-propenyl machine, etc.), a silyl machine, a silyloxy machine, etc. are mentioned.

[0069] The fused salt expressed by the above-mentioned general formula (Y-a) - (Y-c) either may form a polymer through either Qy1, and Ry1-Ry6.

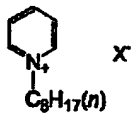
[0070] You may use the fused salt expressed by the above-mentioned general formula (Y-a) - (Y-c) either, mixing with the salt which could use it, having mixed two or more sorts even if it used it independently, and replaced iodide ion I- by other anions. As an anion which replaces I-, halogenide ion, SCN- (Cl-, Br-, etc.), BF4-, PF6-, ClO4-, 2 (CF3SO2)N-, 2 (CF3CF2SO2)N-, CF3SO3-, CH3SO3-, CF3COO-, Ph4B-, 3(CF3SO2) C-, etc. are desirable. They are SCN-, BF4-, CF3SO3-, CF3COO-, or (CF3SO2) 2N- more preferably.

[0071] Moreover, alkali-metal salts, such as other iodine salts and CF3COOLi like LiI, CF3COONa, LiSCN, and NaSCN, can also be added. As for the addition of an alkali-metal salt, it is desirable to consider as a 0.02 - 2 mass % grade, and it is still more desirable to consider as 0.1 to 1 mass %.

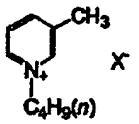
[0072] Although - (Y29) is listed to the example (Y1) of the electrolyte salt preferably used by this invention, and the following, they do not limit this invention.

[0073]

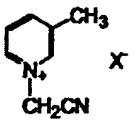
[Formula 27]

(Y1) 

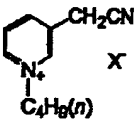
Y1-1 : X⁻=I⁻
Y1-2 : X⁻=BF_4^-
Y1-3 : X⁻=$N^-(SO_2CF_3)_2$
Y1-4 : X⁻=PF_6^-

(Y2) 

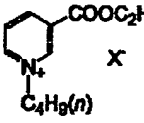
Y2-1 : X⁻=I⁻
Y2-2 : X⁻=BF_4^-
Y2-3 : X⁻=$N^-(SO_2CF_3)_2$
Y2-4 : X⁻=CF_3COO^-
Y2-5 : X⁻=SCN^-
Y2-6 : X⁻=$CF_3SO_3^-$

(Y3) 

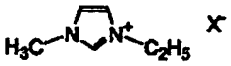
Y3-1 : X⁻=I⁻
Y3-2 : X⁻=BF_4^-
Y3-3 : X⁻=$N^-(SO_2CF_3)_2$

(Y4) 

Y4-1 : X⁻=I⁻
Y4-2 : X⁻=BF_4^-
Y4-3 : X⁻=$N^-(SO_2CF_3)_2$

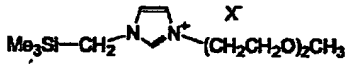
(Y5) 

Y5-1 : X⁻=I⁻
Y5-2 : X⁻=BF_4^-
Y5-3 : X⁻=$N^-(SO_2CF_3)_2$

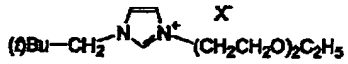
(Y6) 

Y6-1 : X⁻=I⁻
Y6-2 : X⁻=BF_4^-
Y6-3 : X⁻=$N^-(SO_2CF_3)_2$
Y6-4 : X⁻=Br^-
Y6-5 : X⁻=CF_3COO^-
Y6-6 : X⁻=SCN^-
Y6-7 : X⁻=$CF_3SO_3^-$

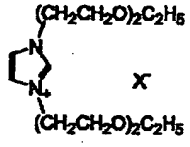
[0074]
[Formula 28]

(Y7) 

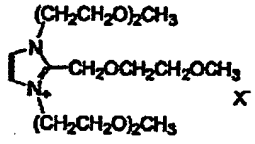
Y7-1 : X⁻=I⁻
Y7-2 : X⁻=BF_4^-
Y7-3 : X⁻=$N^-(SO_2CF_3)_2$
Y7-4 : X⁻=CF_3COO^-
Y7-5 : X⁻=SCN^-

(Y8) 

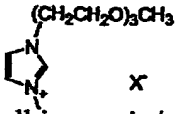
Y8-1 : X⁻=I⁻
Y8-2 : X⁻=BF_4^-
Y8-3 : X⁻=$N^-(SO_2CF_3)_2$
Y8-4 : X⁻=PF_6^-
Y8-5 : X⁻=CF_3COO^-
Y8-6 : X⁻=SCN^-
Y8-7 : X⁻=$CF_3SO_3^-$

(Y9) 

Y9-1 : X⁻=I⁻
Y9-2 : X⁻=BF_4^-
Y9-3 : X⁻=$N^-(SO_2CF_3)_2$
Y9-4 : X⁻=CF_3COO^-
Y9-5 : X⁻=SCN^-
Y9-6 : X⁻=$CF_3SO_3^-$

(Y10) 

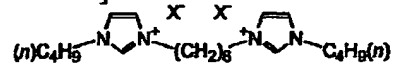
Y10-1 : X⁻=I⁻
Y10-2 : X⁻=BF_4^-
Y10-3 : X⁻=$N^-(SO_2CF_3)_2$

(Y11) 

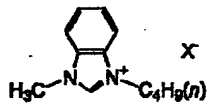
Y11-1 : X⁻=I⁻
Y11-2 : X⁻=BF_4^-
Y11-3 : X⁻=$N^-(SO_2CF_3)_2$

$(CH_2CH_2O)_3CH_3$

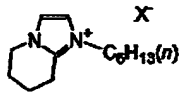
[0075]
[Formula 29]

(Y12) 

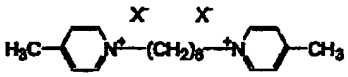
Y12-1 : X^-=I^-
Y12-2 : X^-=BF_4^-
Y12-3 : X^-=$N^-(SO_2CF_3)_2$

(Y13) 

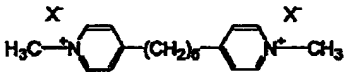
Y13-1 : X^-=I^-
Y13-2 : X^-=BF_4^-
Y13-3 : X^-=$N^-(SO_2CF_3)_2$

(Y14) 

Y14-1 : X^-=I^-
Y14-2 : X^-=BF_4^-
Y14-3 : X^-=$N^-(SO_2CF_3)_2$

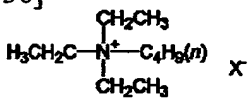
(Y15) 

Y15-1 : X^-=I^-
Y15-2 : X^-=BF_4^-
Y15-3 : X^-=$N^-(SO_2CF_3)_2$

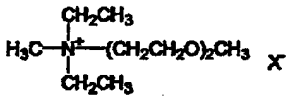
(Y16) 

Y16-1 : X^-=I^-
Y16-2 : X^-=BF_4^-
Y16-3 : X^-=$N^-(SO_2CF_3)_2$

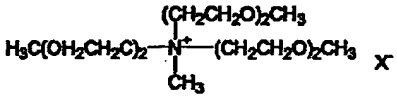
[0076]
[Formula 30]

(Y17) 

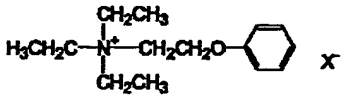
Y17-1 : X^-=I^-
Y17-2 : X^-=BF_4^-
Y17-3 : X^-=$N^-(SO_2CF_3)_2$
Y17-4 : X^-=PF_6^-

(Y18) 

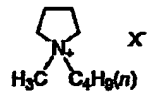
Y18-1 : X^-=I^-
Y18-2 : X^-=BF_4^-
Y18-3 : X^-=$N^-(SO_2CF_3)_2$

(Y19) 

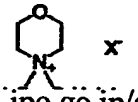
Y19-1 : X^-=I^-
Y19-2 : X^-=BF_4^-
Y19-3 : X^-=$N^-(SO_2CF_3)_2$
Y19-4 : X^-=CF_3COO^-
Y19-5 : X^-=SCN^-
Y19-6 : X^-=$CF_3SO_3^-$

(Y20) 

Y20-1 : X^-=I^-
Y20-2 : X^-=BF_4^-
Y20-3 : X^-=$N^-(SO_2CF_3)_2$

(Y21) 

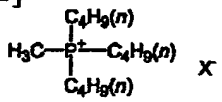
Y21-1 : X^-=I^-
Y21-2 : X^-=BF_4^-
Y21-3 : X^-=$N^-(SO_2CF_3)_2$

(Y22) 

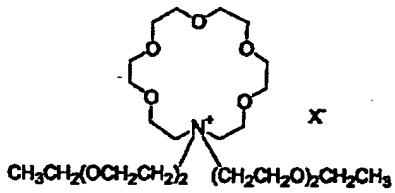
Y22-1 : X^-=I^-
Y22-2 : X^-=BF_4^-
Y22-3 : X^-=$N^-(SO_2CF_3)_2$

H_3C $C_4H_9(n)$

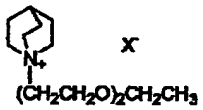
[0077]
[Formula 31]

(Y23) 

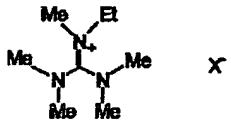
Y23-1 : $X^-=I^-$
Y23-2 : $X^-=BF_4^-$
Y23-3 : $X^-=N^-(SO_2CF_3)_2$

(Y24) 

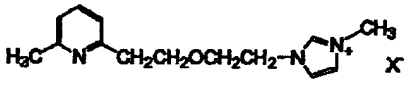
Y24-1 : $X^-=I^-$
Y24-2 : $X^-=BF_4^-$
Y24-3 : $X^-=N^-(SO_2CF_3)_2$

(Y25) 

Y25-1 : $X^-=I^-$
Y25-2 : $X^-=BF_4^-$
Y25-3 : $X^-=N^-(SO_2CF_3)_2$

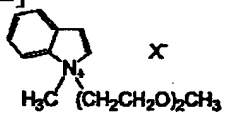
(Y26) 

Y26-1 : $X^-=I^-$
Y26-2 : $X^-=N^-(SO_2CF_3)_2$
Y26-3 : $X^-=BF_4^-$
Y26-4 : $X^-=PF_6^-$

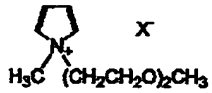
(Y27) 

Y27-1 : $X^-=I^-$
Y27-2 : $X^-=N^-(SO_2CF_3)_2$
Y27-3 : $X^-=BF_4^-$
Y27-4 : $X^-=CF_3COO^-$
Y27-5 : $X^-=SCN^-$
Y27-6 : $X^-=CF_3SO_3^-$

[0078]
[Formula 32]

(Y28) 

Y28-1 : $X^-=I^-$
Y28-2 : $X^-=BF_4^-$
Y28-3 : $X^-=N^-(SO_2CF_3)_2$

(Y29) 

Y29-1 : $X^-=I^-$
Y29-2 : $X^-=BF_4^-$
Y29-3 : $X^-=N^-(SO_2CF_3)_2$

[0079] It is desirable not to use a solvent in this invention using what is in a melting state in ordinary temperature as an electrolyte salt. Although the solvent mentioned later may be added, as for the content of an electrolyte salt, it is desirable that it is more than 50 mass % to the whole electrolyte constituent, and it is desirable that it is especially more than 90 mass %. Moreover, as for the first of this invention, and second electrolyte constituents, it is desirable to contain the above-mentioned siloxane compound and iodine salts other than the above-mentioned polymer, and it is desirable that more than 50 mass % is an iodine salt among the salts to be used. Moreover, when using a solvent, it is desirable to make concentration of an electrolyte salt into 0.05 - 2 mol/l, and considering as 0.1 - 1.5 mol/l is more desirable.

[0080] (E) As for the first of an iodine this invention, and second electrolyte constituents, it is desirable to contain iodine. As for an iodine content, it is desirable that it is 0.1 to 20 mass % to the whole electrolyte constituent, and it is more desirable that it is 0.5 to 5 mass %. Moreover, iodine and a bromine can be added in the reaction solution containing the siloxane compound, electrophilic agent, and electrolyte salt which were mentioned above, and it can also be made to generate a redox couple beforehand. As for the concentration of the iodine in this reaction solution, or a bromine,

considering as 0.01 - 0.3 mol/l is desirable.

[0081] (F) The first of a solvent this invention and second electrolyte constituents may contain the solvent. It is desirable that it is below the whole 50 mass %, as for the solvent content of an electrolyte constituent, it is more desirable that it is below 30 mass %, and it is desirable that it is especially below 10 mass %.

[0082] As a solvent, ionic mobility is high at hypoviscosity, or what can discover the ion conductivity which raised effective carrier concentration with the high dielectric constant, or was excellent since it was the both is desirable. as such a solvent -- a carbonate compound (ethylene carbonate --) Heterocyclic compounds, such as propylene carbonate (3-methyl-2-oxazolidinone etc.), ether compounds (a dioxane, diethylether, etc.) and chain-like ether (ethylene glycol dialkyl ether --) The propylene-glycol dialkyl ether, the polyethylene-glycol dialkyl ether, alcohols (a methanol --), such as the polypropylene-glycol dialkyl ether Ethanol, ethylene glycol monoalkyl ether, propylene-glycol monoalkyl ether, Polyethylene-glycol monoalkyl ether, polypropylene-glycol monoalkyl ether, etc., polyhydric alcohol (ethylene glycol, a propylene glycol, and a polyethylene glycol --) nitryl compounds (an acetonitrile --), such as a polypropylene glycol and a glycerol Guru taro dinitrile, a methoxy acetonitrile, a propionitrile, Ester (a carboxylate, phosphoric ester, phosphonate, etc.), such as a benzonitrile and screw cyano ethyl ether, non-proton nature polar solvents (dimethyl sulfoxide (DMSO), sulfolane, etc.), water, etc. are mentioned. Especially, a carbonate compound, a nitryl compound, and a heterocyclic compound are desirable. These solvents may mix and use two or more sorts if needed.

[0083] (G) In addition, to the first of this invention, and second electrolyte constituents, it is desirable to add basic compounds, such as t-butyl pyridine [of a publication (1997)], 2-picoline, 2, and 6-lutidine, to J.Am.Ceram.Soc., 80 (12), 3157-3171, etc. The desirable density ranges in the case of adding a basic compound are 0.05-2M.

[0084] In order to gel the first and second electrolyte constituents, technique, such as a polymerization of the monomers containing polymer addition, oil gelling agent addition, and polyfunctional monomer and crosslinking reaction of polymer, can be used together. When making it gel by polymer addition, the compound of a publication etc. is usable to "Polymer Electrolyte Reviews -1 and 2" (coeditorship of J.R.MacCallum and C.A.Vincent, ELSEVIER APPLIED SCIENCE), and it is desirable to use a polyacrylonitrile or a polyvinylidene fluoride. When making it gel by oil gelling agent addition, J.Chem.Soc.Japan, Ind.Chem.Sec., 46, and 779 (1943), J.Am.Chem.Soc., 111, and 5542 (1989), J.Chem.Soc., Chem.Commun., 1993, 390, Angew.Chem.Int.Ed.Engl., 35, and 1949 (1996), It is desirable to use the compound which can use the compound indicated by Chem.Lett., 1996, 885, J.Chem.Soc., Chem.Commun., 1997, and 545 grades, and has amide structure. Moreover, the method of gelling the electrolytic solution given in JP,11-185863,A and the method of gelling the quality of molten salt electrolysis given in JP,2000-58140,A are also applicable to this invention. moreover, the case where an electrolyte constituent is made to gel by the crosslinking reaction of polymer -- JP,2000-17076,A -- said -- the cross linking technique indicated by 2000-86724 is also applicable

[0085] [2] The optoelectric transducer of an optoelectric-transducer this invention has a conductive layer, a photosensitive layer, a charge transporting bed, and a counter electrode. As preferably shown in drawing 1 , a laminating is carried out to the order of a conductive layer 10, an under coat 60, a photosensitive layer 20, the charge transporting bed 30, and the counter electrode conductive layer 40, and a photosensitive layer 20 consists of charge transportation material 23 which permeated the opening between the semiconductor particle 21 by which sensitization was carried out with coloring matter 22, and the semiconductor particle 21 concerned. The charge transportation material 23 consists of the same component as the material used for the charge transporting bed 30. Moreover, in order to give intensity to an optoelectric transducer, you may form a substrate 50 as a ground of a conductive layer 10 and/or the counter electrode conductive layer 40. In this invention, it is arbitrary and the layer which consists the layer which consists of a conductive layer 10 and a substrate 50 to prepare of "a conductive base material", a counter electrode conductive layer 40, and a substrate 50 that it is arbitrary and is prepared is called "counter electrode." In addition, the conductive layer 10 in drawing 1 , the counter electrode conductive layer 40, and a substrate 50 may be transparent

conductive-layer 10a, transparent counter electrode conductive-layer 40a, and transparent substrate 50a, respectively. That to which this optoelectric transducer is connected to an external load, and electric work (power generation) is done is a photoelectric cell, and it is the photosensor which was made for the purpose of sensing of optical information.

[0086] In the optoelectric transducer of this invention shown in drawing 1 , when a semiconductor particle is n type, the light which carried out incidence to the photosensitive layer 20 containing the semiconductor particle 21 by which sensitization was carried out with coloring matter 22 excites coloring matter 22, and the electron of the high energy in the excited coloring matter 22 is passed to the conduction band of the semiconductor particle 21, and it reaches a conductive layer 10 by diffusion further. At this time, coloring matter 22 serves as an oxidant. In a photoelectric cell, while the electron in a conductive layer 10 works in an external circuit, it returns to the oxidant of coloring matter 22 through the counter electrode conductive layer 40 and the charge transporting bed 30, and coloring matter 22 is reproduced. A photosensitive layer 20 works as a negative electrode (optical anode), and a counter electrode 40 commits it as a positive electrode. On the boundaries (for example, the boundary of a conductive layer 10 and a photosensitive layer 20, the boundary of a photosensitive layer 20 and the charge transporting bed 30, the boundary of the charge transporting bed 30 and the counter electrode conductive layer 40, etc.) of each layer, the constituents of each class may be carrying out diffusive mixing mutually. Hereafter, each class is explained in detail.

[0087] (A) A conductive base material conductivity base material consists of the monolayer of (1) conductive layer or (2) conductive layers, and two-layer [of a substrate]. In the case of (1), that at which intensity and sealing performance are fully maintained as a material of a conductive layer can be used, for example, it can use metallic materials (platinum, gold, silver, copper, zinc, titanium, aluminum, these alloys, etc.). In the case of (2), the substrate which has a conductive layer containing an electric conduction agent can be used for a photosensitive-layer side. As a desirable electric conduction agent, metals (for example, platinum, gold, silver, copper, zinc, titanium, aluminum, an indium, the alloy containing these, etc.), carbon, and conductive metallic oxides (what doped a fluorine or antimony to an indium-tin multiple oxide and the tin oxide) are mentioned. The thickness of a conductive layer has desirable about 0.02-10 micrometers.

[0088] A conductive base material has surface electrical resistance as good as a low. Surface electrical resistance is below 50ohms / ** preferably, and is below 20ohms / ** more preferably.

[0089] When irradiating light from a conductive base material side, as for a conductive base material, it is desirable that it is substantially transparent. It means substantially that a light transmittance is it 10% or more that it is transparent in some or the whole region of a visible - near infrared region (400-1200nm). As for this light transmittance, it is desirable that it is 50% or more, and it is more desirable that it is 80% or more. It is desirable that the light transmittance of the wavelength region where a photosensitive layer has sensitivity especially is high.

[0090] What formed the transparent conductive layer which consists of a conductive metallic oxide in the front face of transparent substrates, such as glass and plastics, by an application or vacuum evaporationo as a transparent conductivity base material is desirable. As for a transparent conductive layer, it is desirable to consist of diacid-ized tin which doped a fluorine or antimony, or an indium-stannic-acid ghost (ITO). In addition to glass substrates, such as an advantageous soda glass and an alkali free glass without the influence of alkali elution, as a transparent substrate, a transparent polymer film is usable in respect of cost and intensity. As a material of a transparent polymer film, a triacetyl-cellulose (TAC), polyethylene-terephthalate (PET), polyethylenenaphthalate (PEN), syndiotactic polystyrene (SPS), polyphenylene-sulfide (PPS), polycarbonate (PC), polyarylate (PAr), polysulfone (PSF), polyester sulfone (PES), polyimide (PI), polyether imide (PEI), annular polyolefine, and bromine-ized phenoxy etc. is usable. In order to secure sufficient transparency, as for the coverage of a conductive metallic oxide, it is desirable to consider as per [0.01-100g] two 1m of base materials of glass or plastics.

[0091] It is desirable to use a metal lead in order to lower resistance of a transparent conductivity base material. The quality of the material of a metal lead has desirable metals, such as platinum, gold, nickel, titanium, aluminum, copper, and silver. As for a metal lead, it is desirable to install in a transparent substrate by vacuum evaporationo, sputtering, etc., and to prepare on it the transparent

conductive layer which consists of conductive tin oxide or ITO. The fall of the amount of incident lights by metal lead installation is more preferably suppressed to 1 - 5% less than 10%.
[0092] (B) As for a photosensitive-layer (1) semiconductor photosensitive layer, it is desirable to contain the semiconductor particle by which sensitization was carried out with coloring matter. In a photosensitive layer, a semiconductor acts as a photo conductor, absorbs light, performs charge separation, and produces an electron and an electron hole. With the semiconductor by which coloring matter sensitization was carried out, generating of an optical absorption, the electron by this, and an electron hole takes place mainly in coloring matter, and a semiconductor bears the role which receives and transmits this electron (or electron hole). As for the semiconductor used by this invention, it is desirable that it is the n-type semiconductor which a conductor electron serves as a carrier under optical pumping, and gives an anode current.
[0093] The compounds (a strontium titanate, titanic-acid calcium, titanic-acid sodium, a barium titanate, niobic-acid potassium, etc.) which have an element semiconductor like silicon or germanium, a III-V system compound semiconductor, metaled chalcogenide (an oxide, a sulfide, selenides, those composites, etc.), and a perovskite structure as an example of the semiconductor used by this invention are mentioned. Metal chalcogenide is desirable especially.
[0094] As desirable metal chalcogenide, the oxide of titanium, tin, zinc, iron, a tungsten, a zirconium, a hafnium, strontium, an indium, a cerium, an yttrium, a lanthanum, vanadium, niobium, or a tantalum, cadmium, zinc, lead, silver, antimony or the sulfide of a bismuth, cadmium or a leaden selenide, the telluride of cadmium, etc. are mentioned. As other compound semiconductors, the selenide of phosphides, such as zinc, a gallium, an indium, and cadmium, a gallium arsenide, or a copper-indium, the sulfide of a copper-indium, etc. are mentioned. Furthermore, a composite like MxOySz or M1xM2yOz (an oxygen atom, x, and y and z express the number [atom / metal] with which M, M1, and M2 become, and, as for O, a valence becomes neutral, respectively) can also be used preferably.
[0095] Preferably the semiconductor used by this invention Si, TiO2, SnO2, Fe 2O3, WO3, ZnO, Nb 2O5, CdS, ZnS and PbS, Bi2S3, CdSe, CdTe, It is SrTiO3, GaP, InP, GaAs, CuInS2, or CuInSe2. More preferably TiO2, SnO2, Fe 2O3, WO3, ZnO, It is Nb 2O5, CdS and PbS, CdSe, SrTiO3 and InP, GaAs, CuInS2, or CuInSe2, is TiO2 or Nb 2O5 especially preferably, and is TiO2 most preferably. As for TiO2, it is desirable to include an anatase type crystal 70% or more, and it is more desirable that it is 100% anatase type crystal.
[0096] It is desirable to dope a metal in order to raise the electronic conductivity in a semiconductor. As a metal to dope, a divalent or trivalent metal is desirable. In order to prevent that a reverse current flows from a semiconductor to a charge transporting bed, it is also effective in a semiconductor to dope a univalent metal.
[0097] Although a single crystal or a polycrystal is sufficient as the semiconductor used for this invention, the polycrystal from a viewpoint of a manufacturing cost, raw-material reservation, and an energy pay back time is desirable. The amorphous portion may be included in part. As for a semiconductor, it is desirable to use as a porous membrane which consists of a semiconductor particle.
[0098] Generally the particle size of a semiconductor particle is the order of nm-mu m. As for the primary-particle mean particle diameter which asked for the projected area of a particle from the diameter when converting into a circle, it is desirable that it is 5-200nm, and it is more desirable that it is 8-100nm. Moreover, as for the mean particle diameter of the semiconductor particle in the dispersion liquid produced in order to apply on a conductive base material (aggregated particle), it is desirable that it is 0.01-30 micrometers. Two or more kinds of particles from which a particle size distribution differs may be mixed, it is desirable that the average size of a small particle is 25nm or less in this case, and it is more desirable that it is 10nm or less. Particle size is big, for example, it is also desirable to mix a semiconductor particle (100nm or more and about 300nm) in order to scatter an incident light and to raise the rate of optical capture.
[0099] You may mix and use two or more sorts of semiconductor particles from which a kind also differs. In such a case, as for one sort, it is desirable that they are TiO2, ZnO, Nb 2O5, or SrTiO3. As for another side, it is desirable that they are SnO2, Fe 2O3, or WO3. Especially, ZnO, SnO2, ZnO and

WO3, ZnO, or the combination of SnO2 and WO3 is more desirable. When mixing and using two or more sorts of semiconductor particles, each particle size may differ. Especially the particle size of the above Nb [TiO2, ZnO, and] 2O5 or SrTiO3 is large, and its small one is [the particle size of SnO2, Fe 2O3, or WO3] desirable. The large particle and large particle size of 100nm or more have [particle size] a desirable combination of a small particle 15nm or less.

[0100] a sol-gel method given [as a method of producing a semiconductor particle] in "the thin-layer-coating technology by the sol-gel method" (1995) etc. of the company (1998) of the "science of sol-gel method" AGUNE ** style of ********, and a technical-information association, and "composition of the monodisperse particle by the new synthesis method gel-sol method and size form control" of Tadao Sugimoto -- wait -- the gel-sol method given in ****, the 35th volume, No. 9, 1012-1018 etc. pages (1996), Moreover, the method of producing an oxide for the chloride which Degussa developed by elevated-temperature hydrolysis in an acid hydrogen salt is also preferably applicable.

[0101] When a semiconductor particle is titanium oxide, each of above-mentioned sol-gel methods, gel-sol methods, and elevated-temperature adding-water part solution methods in the inside of the acid hydrogen salt of a chloride can be used preferably, and may use the sulfuric-acid method and chlorine method of a publication for "titanium oxide physical-properties and applied-technology" Gihodo Shuppan Co., Ltd. (1997) of the Seino study further. In addition, a sol-gel method given in Barbe's and others journal OBU American ceramic society, the 80th volume, No. 12, 3157-3171 pages (1997), Burnside's and others chemical MATERIARUZU, the 10th volume, No. 9, 2419-2425 etc. pages, etc. is also desirable.

[0102] (2) In case a semiconductor particle layer semiconductor particle is applied on a conductive base material, in addition to the method of applying the dispersion liquid or the colloidal solution of a semiconductor particle on a conductive base material, the above-mentioned sol-gel method etc. can be used. When mass-production-izing of an optoelectric transducer, the physical properties of semiconductor particle dispersion liquid, the versatility of a conductive base material, etc. are taken into consideration, the wet film production method is comparatively desirable. As the wet film production method, the applying method, print processes, an electrolytic-deposition method, and an electrodeposition process are typical. Moreover, you may use the SPD method which sprays the metallic-oxide precursor pyrolyzed on the method of carrying out vacuum evaporationo by the method (the LPD method) of depositing by the liquid phase by the ligand exchange etc., the spatter, etc., CVD, or the warmed substrate from the method of oxidizing a metal, and a metal solution, and forms a metallic oxide.

[0103] In case the method and semiconductor which are distributed while grinding as a method of producing the dispersion liquid of a semiconductor particle using the above-mentioned sol-gel method, the method of mashing with a mortar, and a mill are compounded, the method of depositing as a particle and using it as it is in a solvent, etc. is mentioned.

[0104] As a dispersion medium, water or various kinds of organic solvents (for example, a methanol, ethanol, isopropyl alcohol, a citronellol, terpineol, a dichloromethane, an acetone, an acetonitrile, ethyl acetate, etc.) are usable. In case it distributes, you may use polymer, such as a polyethylene glycol, a hydroxyethyl cellulose, and a carboxymethyl cellulose, a surfactant, an acid, a chelating agent, etc. as a distributed assistant if needed. Especially, it is desirable to add a polyethylene glycol. By changing the molecular weight of the polyethylene glycol to add, the viscosity of dispersion liquid can be adjusted, the semiconductor layer which cannot separate easily can be formed or the voidage of a semiconductor layer can be controlled.

[0105] As the desirable method of application, the method by which application and metering, such as the slide hopper method given in metering systems, such as application systems, such as a roller and the dipping method, the air knife method, and the blade method, the wire bar method given in JP,58-4589,B, U.S. JP,2681294,B, said 2761419 numbers, said 2761791 numbers, etc., the extrusion method, and the curtain method, are made into the same portion is mentioned. Moreover, the spin method and a spray method are also desirable as a general aviation. As the wet printing method, intaglio printing, the rubber version, the screen-stencil including letterpress, offset, and the three major print processes of gravure, etc. can use preferably. What is necessary is just to choose the

desirable film production method according to liquid viscosity or wet thickness from the above methods.

[0106] A semiconductor particle layer can carry out the multilayer application of the semiconductor particle dispersion liquid from which not only a monolayer but particle size differs, or can also carry out the multilayer application of the layer containing the semiconductor particles (or a different binder, a different additive, etc.) of a different kind. The multilayer application is effective when thickness runs short by application once.

[0107] Although the rate of capture of light generally becomes high since the amount of coloring matter support per unit projected area increases so that semiconductor particle layer thickness (it is the same as the thickness of a photosensitive layer) becomes thick, since the generated diffusion length of electron increases, the loss by charge reunion also becomes large. Therefore, the thickness with a desirable semiconductor particle layer is 0.1-100 micrometers. When using for a photoelectric cell, as for semiconductor particle layer thickness, it is desirable that it is 1-30 micrometers, and it is more desirable that it is 2-25 micrometers. As for the semiconductor particle coverage per two, it is desirable to be referred to as 0.5-100g, and it is [1m of base materials] more desirable to be referred to as 3-50g.

[0108] Heat-treating is desirable in order to raise paint film intensity and adhesion with a base material while contacting semiconductor particles electronically, after applying a semiconductor particle to a conductive base material. As for heating temperature, it is desirable to consider as 40 degrees C or more less than 700 degrees C, and it is more desirable to consider as 100 degrees C or more 600 degrees C or less. Moreover, what is necessary is just to make heating time into 10 minutes - about 10 hours. When using a base material with low melting point and softening temperature like a polymer film, the heat-treatment in an elevated temperature is not desirable in order to cause degradation of a base material. Moreover, it is desirable to perform heat-treatment as much as possible also from a viewpoint of cost reduction at low temperature (for example, 50 degrees C - 350 degrees C). Low temperature-ization of heat-treatment temperature is attained by using together a semiconductor particle with a particle size of 5nm or less mentioned above, or heat-treating under existence of a mineral-acid metallurgy group oxide precursor. Moreover,-izing can be carried out [low temperature] by impressing irradiation, the electric field, or the ultrasonic wave of ultraviolet rays, infrared radiation, microwave, etc. It is desirable to use together suitably heating, reduced pressure, oxygen plasma treatment, pure water washing, solvent cleaning, gas scrubbing, etc. for the purpose which removes the unnecessary organic substance etc. in addition to the above-mentioned irradiation etc.

[0109] After heat-treatment, in order to increase the surface area of a semiconductor particle, or in order to raise the purity near the semiconductor particle and to raise the electron-injection efficiency from coloring matter to a semiconductor particle, you may perform chemical-plating processing using titanium-tetrachloride solution, and electrochemical plating processing using titanium-trichloride solution. Moreover, in order to prevent that a reverse current flows from a semiconductor particle to a charge transporting bed, it is effective in a particle front face to also make the low organic substance of electronic conductivity other than coloring matter adsorb. As for the organic substance made to adsorb, it is desirable to have a hydrophobic radical.

[0110] As for a semiconductor particle layer, it is desirable to have a big surface area so that much coloring matter can be adsorbed. As for the surface area in the state where the semiconductor particle was applied on the base material, it is desirable that they are 10 or more times to projected area, and it is more desirable that they are 100 or more times. Although especially a limit is infinite, they are usually about 1000 times.

[0111] (3) That what is necessary is just what has absorption in a visible region or a near-infrared region, and can carry out sensitization of the semiconductor, the coloring matter used for a coloring matter photosensitive layer is metal complex coloring matter, methine coloring matter, porphyrin system coloring matter, and/or phthalocyanine system coloring matter preferably, and is metal complex coloring matter and/or poly methine coloring matter especially preferably. In order to make the wavelength region of photo electric translation large as much as possible and to gather a conversion efficiency, you may use together two or more kinds of coloring matter. In this case, what

is necessary is just to choose the coloring matter used together and its mixed rate according to the wavelength region and intensity distribution of the light source.

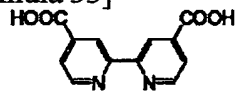
[0112] The coloring matter used by this invention has the suitable joint machine (interlocking group) which has the adsorption capacity force to a semiconductor particle front face preferably. The chelation machine which has pi conductivity like -COOH basis, -OH basis, -SO3H set, -P(O) (OH)2 set, an acidic group like -OP(O) (OH)2 set and an oxime, dioxime, a hydroxyquinoline, salicylate, and alpha-KETOENO rate as a desirable joint machine is mentioned. -COOH basis, -P(O) (OH)2 set, and especially -OP(O) (OH)2 set are desirable especially. These joint machines may form alkali metal etc. and the salt, and may form the inner salt. Moreover, in poly methine coloring matter, it is good also considering the oak which contains an acidic group like [in case a methine chain forms a squarylium ring and a crocodile NIUMU ring], and this portion as a joint machine. Hereafter, the desirable sensitizing dye used for a photosensitive layer is explained concretely.

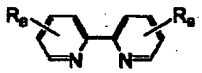
[0113] (a) As for the metal complex coloring matter used by the metal complex coloring matter this invention, it is desirable that they are metal phthalocyanine dye or metalloporphyrin coloring matter. Moreover, the metal atom of metal complex coloring matter has desirable Ruthenium Ru. as the ruthenium complex coloring matter which can be used by this invention -- for example, U.S. JP,4927721,B -- said -- No. 4684537 -- said -- No. 5084365 -- said -- No. 5350644 -- said -- No. 5463057 -- said -- the thing of a publication is mentioned to No. 5525440, JP,7-249790,A, ****** No. 504512 [ten to], the world patent 98/No. 50393, JP,2000-26487,A, etc.

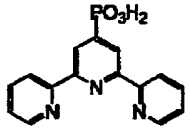
[0114] The ruthenium complex coloring matter used by this invention is following (general formula I):(A1) pRu (B-a) (B-b) (B-c). ... Being expressed by (I) is desirable. Among a general formula (I), A1 expresses the ligand of 1 or 2 seats, and expresses the ligand chosen from the group which consists of a derivative of Cl, SCN, H2O, Br, I, CN and NCO, SeCN and beta-diketones, oxalic acid, and a dithiocarbamic acid. p is the integer of 0-3. B-a, B-b, and B-c express the organic ligand chosen from the compound independently expressed by the following formula B-1 to B-10, respectively.

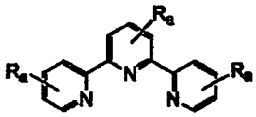
[0115]

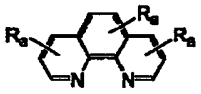
[Formula 33]

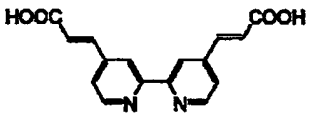
B-1 

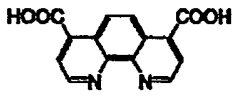
B-2 

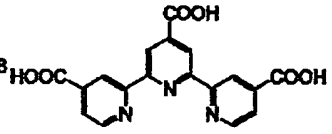
B-3 

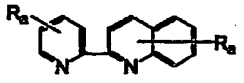
B-4 

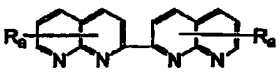
B-5 

B-6 

B-7 

B-8 

B-9 

B-10 

[0116] Ra expresses a hydrogen atom or a substituent among a formula B-1 to B-10. As an example

of this substituent, the aryl group which is not replaced [the substitution of the aralkyl machine which is not replaced / the substitution of the alkyl group which is not replaced / the substitution of a halogen atom and the carbon atomic numbers 1-12 or / and the carbon atomic numbers 7-12 or / and the carbon atomic numbers 6-12 or], the above-mentioned acidic group (you may form the salt), and a chelation machine are mentioned. Here, the shape of a straight chain and the letter of branching are sufficient as the alkyl portions of an alkyl group and an aralkyl machine, and a monocycle or a polycyclic (the condensed ring, ring set) is sufficient as the aryl portions of an aryl group and an aralkyl machine. Even if B-a, B-b, and B-c are the same, they may differ from each other, and any one or two are sufficient as them.

[0117] Although the desirable example of the metal complex coloring matter which can be used by this invention is shown below, this invention is not limited to these.

[0118]

[Formula 34]

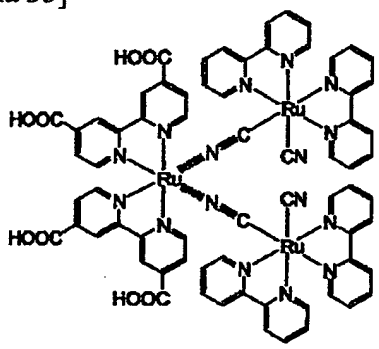
$(A_1)_pRu(B\text{-}a)(B\text{-}b)(B\text{-}c)$ ・・・ (I)

	A_1	p	B-a	B-b	B-c	R_a
R-1	SCN	2	B-1	B-1	—	—
R-2	CN	2	B-1	B-1	—	—
R-3	Cl	2	B-1	B-1	—	—
R-4	CN	2	B-7	B-7	—	—
R-5	SCN	2	B-7	B-7	—	—
R-6	SCN	2	B-1	B-2	—	H
R-7	SCN	1	B-1	B-3	—	—
R-8	Cl	1	B-1	B-4	—	H
R-9	I	2	B-1	B-5	—	H
R-10	SCN	3	B-8	—	—	—
R-11	CN	3	B-8	—	—	—
R-12	SCN	1	B-2	B-8	—	H
R-13	—	0	B-1	B-1	B-1	—

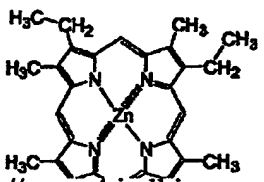
[0119]

[Formula 35]

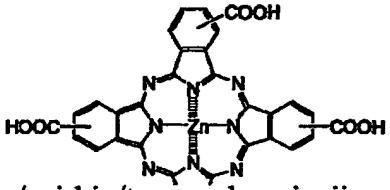
R-14



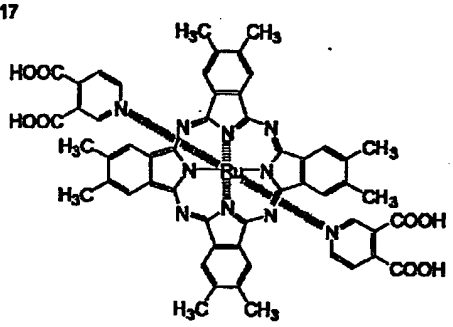
R-15



R-16



R-17

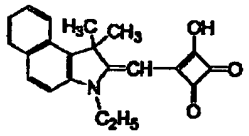


[0120] (b) The methine coloring matter used by the methine coloring matter this invention is poly methine coloring matter, such as a cyanine dye, merocyanine coloring matter, and SUKUWARIRIUMU coloring matter, preferably. As poly methine coloring matter, the thing of a publication can be used for JP,11-35836,A, JP,11-67285,A, JP,11-86916,A, JP,11-97725,A, JP,11-158395,A, JP,11-163378,A, JP,11-214730,A, JP,11-214731,A, JP,11-238905,A, JP,2000-26487,A, the Europe patent No. 892411, said 911841 numbers, and said 991092 numbers. The example of desirable methine coloring matter is shown below.

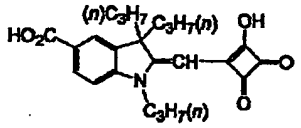
[0121]

[Formula 36]

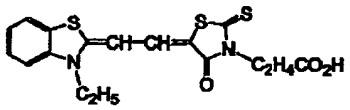
M-1



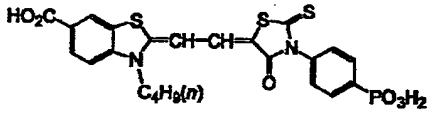
M-2



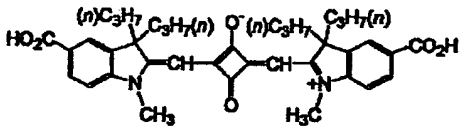
M-3



M-4



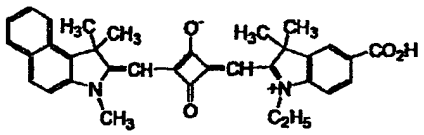
M-5



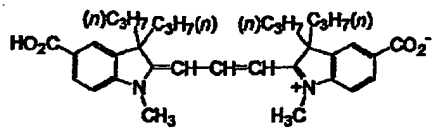
[0122]

[Formula 37]

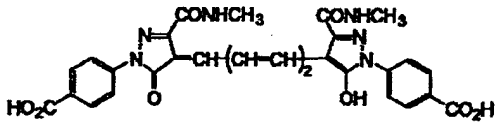
M-6



M-7

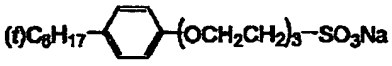


M-8



[0123] (4) In order to make coloring matter stick to the adsorption semiconductor particle of the coloring matter to a semiconductor particle, the method immersed into the solution of coloring matter in the conductive base material which has the often dried semiconductor particle layer, or the method of applying the solution of coloring matter to a semiconductor particle layer can be used. By the former method, dip coating, the dipping method, a roller, the air knife method, etc. are usable. In addition, in the case of dip coating, adsorption of coloring matter may be performed at a room temperature, and you may perform it by carrying out heating reflux as indicated by JP,7-249790,A. Moreover, as the latter method, there are the methods of application, such as the wire bar method, the slide hopper method, the extrusion method, the curtain method, the spin method, and a spray method.

[0124] the solvent used for the solution of coloring matter -- the solubility of coloring matter etc. -- responding -- suitably -- it can choose -- for example, alcohols (a methanol --) nitril (an acetonitrile --), such as ethanol, t-butanol, and benzyl alcohol Nitromethanes, such as a propionitrile and 3-methoxy propionitrile, a halogenated hydrocarbon (a dichloromethane, a dichloroethane, and chloroform --) Ether, such as a chlorobenzene (diethylether, tetrahydrofuran, etc.), dimethyl sulfoxide and amides (N.N-dimethylformamide --) N-methyl pyrrolidones, such as N and N-dimethyl acetamido, 1, 3-dimethyl imidazolidinone, 3-methyl oxazolidinone and ester (ethyl acetate, butyl acetate, etc.) Carbonates (diethyl carbonate, an ethylene carbonate, propylene carbonate, etc.), ketones, hydrocarbons (an acetone, 2-butanone, cyclohexanone, etc.) (Korean geisha, the petroleum ether, benzene, toluene, etc.), these mixed solvents, etc. can be used.
[0125] As for all the amounts of adsorption of coloring matter, it is desirable to be referred to as per [a unit surface area (1m2) / 0.01] - 100mmol of a conductive base material. Moreover, in order to acquire sufficient sensitization effect, as for the amount of adsorption to the semiconductor particle of coloring matter, it is desirable that they are per [0.01] 1g of semiconductor particles - 1mmol. The sensitization effect becomes inadequate, and if there is too little amount of adsorption of coloring matter, if many [too], coloring matter will tend to float, and it becomes the cause of reducing the sensitization effect. Moreover, it is desirable to heat-treat, before adsorbing in order to increase the amount of adsorption of coloring matter. In order to suppress that water sticks to a semiconductor particle front face after heat-treatment, it is desirable not to return to ordinary temperature but to make coloring matter adsorb quickly at 60-150 degrees C. Moreover, you may carry out the coadsorption of the colorless compound to a semiconductor particle for the purpose which reduces the interaction of the coloring matter like condensation. As a compound which carries out a coadsorption, a surface activity compound is effective, and surface activity compounds, such as sulfonates shown in the steroid compound (for example, chenodeoxycholic acid) which has a carboxyl group, or the following, can be used.
[0126]
[Formula 38]



[0127] As for non-adsorbed coloring matter, it is desirable that washing removes promptly after adsorption. It is desirable to perform washing in a wet washing tub using organic solvents, such as polar solvents, such as an acetonitrile, and an alcohols solvent. After adsorbing coloring matter, amines and quarternary ammonium salt may be used and the front face of a semiconductor particle may be processed, in order to promote removal of excessive coloring matter. As desirable amines, a pyridine, a 4-t-butyl pyridine, a polyvinyl pyridine, etc. are mentioned. As desirable quarternary ammonium salt, TETORO butyl ammonium iodide, tetrapod hexyl ammonium iodide, etc. are mentioned. These may be dissolved and used for an organic solvent and, in the case of a liquid, you may use as it is.

[0128] (C) A charge transporting-bed charge transporting bed has the function to supplement the oxidant of coloring matter with an electron. Although the first electrolyte constituent of the above-mentioned this invention or the second electrolyte constituent is used for a charge transporting bed, you may use together a solid electrolyte and electron hole (hole) transportation material further.

[0129] A charge transporting bed can form a reaction solution layer on an electrode by the cast method, the applying method, dip coating, the sinking-in method, the penetration method, etc., and, subsequently can be installed by performing the above-mentioned polymerization reaction. Although what is necessary is just to choose heating temperature according to the heat-resistant temperature of the coloring matter to be used when heating and carrying out a polymerization, 10-200 degrees C is more preferably made into 30-150 degrees C. Although heating time is based on heating temperature etc., you may be 5 minutes - about 72 hours.

[0130] Two kinds of methods are possible in detail about the formation method of a charge transporting bed. One is the method of sticking a counter electrode previously on a photosensitive layer, and putting the above-mentioned reaction solution layer between the gap. Another is the method of forming a direct charge transporting bed on a photosensitive layer, and installing a counter electrode after that. In the former method, a reaction solution layer can be put according to the ordinary-pressure process using the capillarity by being immersed etc., or the vacuum process which makes it a low pressure and replaces the gaseous phase of a gap by the liquid phase from an ordinary pressure. What is necessary is to give a counter electrode with not drying and just to take a liquid disclosure prevention measure against the edge section in the latter method, when using a wet electrolyte constituent. What is necessary is just to solidify, after applying a liquefied electrolyte constituent, when using a gel electrolyte. Moreover, when using wet organic electron hole transportation material and a gel electrolyte, the method of forming the above-mentioned photosensitive layer and the same method can be used.

[0131] When using the electron hole (hole) transportation material of a solid electrolyte or a solid-state, a charge transporting bed can be formed by the dry forming-membranes methods, such as a vacuum deposition method and CVD, and a counter electrode can be given after that. An organic electron hole transportation material can be introduced by technique, such as a vacuum deposition method, the cast method, the applying method, the spin coat method, dip coating, an electrolytic polymerization method, and the photoelectrical depolymerizing method. Also in an inorganic solid-state compound, it can introduce by technique, such as the cast method, the applying method, the spin coat method, dip coating, an electrolytic-deposition method, and an electroless deposition method.

[0132] In order to make a redox couple generate, when introducing iodine etc. into a charge transporting bed, the technique of placing [technique] this into an airtight container and diffusing it in an electrolyte with iodine etc., etc. can be used after formation of the method of adding in an electrolytic solution, and a charge transporting bed. Moreover, it is also possible to introduce iodine etc. into the below-mentioned counter electrode into a charge transporting bed, an application or when it carries out vacuum evaporationo and an optoelectric transducer is assembled.

[0133] It is 2,000 ppm or less that it is 10,000 ppm or less desirable still more preferably, and the moisture in a charge transporting bed is 100 ppm or less especially preferably.

[0134] (D) A counter electrode counter electrode acts as a positive electrode, when an optoelectric transducer is used as a photoelectric cell. The counter electrode may consist of only counter electrode conductive layers which consist of a conductive material like the above-mentioned conductive base material, and may consist of a counter electrode conductive layer and a support substrate. As a conductive material used for a counter electrode conductive layer, a metal, carbon (for example, platinum, gold, silver, copper, aluminum, magnesium, an indium, etc.), and conductive metallic oxides (what doped the fluorine to an indium-tin multiple oxide and the tin oxide) are mentioned. Platinum, gold, silver, copper, aluminum, and magnesium are desirable especially. The support substrate used for a counter electrode is a glass substrate or a plastic plate preferably, and the vacuum evaporationo of it is applied or carried out, and it uses the above-mentioned conductive material for this. Although especially the thickness of a counter electrode conductive layer is not restricted, it is desirable that it is 3nm - 10 micrometers. The surface electrical resistance of a counter electrode is as good as a low, it is desirable that they are below 50ohms / **, and it is more desirable that they are below 20ohms / **.

[0135] Since light may be irradiated from both a conductive base material, and both [either or], in order for light to reach a photosensitive layer, it is good if at least one side is substantially transparent among a conductive base material and a counter electrode. It is desirable to make a conductive base material transparent from a viewpoint of the improvement in a generating efficiency, and to carry out incidence of the light from a conductive base material side. In this case, as for a counter electrode, it is desirable to have the property to reflect light. As a material of such a counter electrode, the glass which deposited the metal and the conductive oxide or plastics, a metal thin film, etc. can be used.

[0136] On a charge transporting bed, a counter electrode may stick the application, plating, or conductive-layer side of the substrate which carries out vacuum evaporationo (PVD, CVD), or has a conductive layer, and may prepare direct electric conduction material. Moreover, as well as the case of a conductive base material when especially a counter electrode is transparent, it is desirable to use a metal lead in order to lower resistance of a counter electrode. In addition, the fall of the desirable quality of the material of a metal lead and the desirable installation method, and the amount of incident lights by metal lead installation etc. is the same as the case of a conductive base material.

[0137] (E) In order to prevent other layer counter electrodes and the short circuit of a conductive base material, it is desirable to paint the thin film layer of a conductive base material and a semiconductor precise between photosensitive layers as an under coat beforehand. It is effective especially when using electronic transportation material and electron hole transportation material for a charge transporting bed. The material of an under coat is TiO2, SnO2, Fe 2O3, WO3 and ZnO, and/or Nb 2O5 preferably, and is TiO2 still more preferably. An under coat can be painted by Electrochimi.Acta, 40, the spray pyrolysis method indicated by 643-652 (1995), the spatter, etc. As for the thickness of an under coat, it is desirable that it is 5-1000nm, and it is more desirable that it is 10-500nm.

[0138] Moreover, you may prepare functional layers, such as a protective layer and an acid-resisting layer, between either the conductive base material which acts as an electrode or a counter electrode both outside front faces, a conductive layer, and substrates, or in the middle of a substrate. According to the quality of the material, the applying method, a vacuum deposition, the sticking method, etc. can be used for formation of such a functional layer.

[0139] (F) the example of the internal structure of an optoelectric transducer -- as mentioned above, double the internal structure of an optoelectric transducer with the purpose, and various gestalten are possible for it If it roughly divides into two, the structure in which the incidence of both sides to light is possible, and structure possible only from one side are possible. The internal structure of an optoelectric transducer preferably applicable to drawing 2 - drawing 8 at this invention is illustrated.

[0140] The structure shown in drawing 2 is structure in which a photosensitive layer 20 and the charge transporting bed 30 are made to intervene between transparent conductive-layer 10a and transparent counter electrode conductive-layer 40a, and light carries out incidence from both sides. The structure shown in drawing 3 is structure in which establishes the metal lead 11 in part on

transparent substrate 50a, prepares transparent conductive-layer 10a on it, forms an under coat 60, a photosensitive layer 20, the charge transporting bed 30, and the counter electrode conductive layer 40 in this order, and arranges the support substrate 50 further, and light carries out incidence from a conductive-layer side. The structure shown in drawing 4 is structure in which carries out the metal lead 11 side inside, and arranges transparent substrate 50a which installed the conductive layer 10 further on the support substrate 50, formed the photosensitive layer 20 through the under coat 60, prepared the charge transporting bed 30 and transparent counter electrode conductive-layer 40a further, and established the metal lead 11 in part, and light carries out incidence from a counter electrode side. A part of structure shown in drawing 5 is structure in which prepare transparent conductive-layer 10a and transparent counter electrode conductive-layer 40a on two transparent substrates 50a which established the metal lead 11, respectively, an under coat 60, a photosensitive layer 20, and the charge transporting bed 30 are made to intervene among them, and light carries out incidence from both sides. The structure shown in drawing 6 is structure in which installs transparent conductive-layer 10a on transparent substrate 50a, forms a photosensitive layer 20 through an under coat 60, forms the charge transporting bed 30 and the counter electrode conductive layer 40 further, and arranges the support substrate 50 on this, and light carries out incidence from a conductive-layer side. The structure shown in drawing 7 is structure in which installs a conductive layer 10 on the support substrate 50, forms a photosensitive layer 20 through an under coat 60, prepares the charge transporting bed 30 and transparent counter electrode conductive-layer 40a further, and arranges transparent substrate 50a on this, and light carries out incidence from a counter electrode side. The structure shown in drawing 8 is structure in which installs transparent conductive-layer 10a on transparent substrate 50a, forms a photosensitive layer 20 through an under coat 60, prepares the charge transporting bed 30 and transparent counter electrode conductive-layer 40a further, and arranges transparent substrate 50a on this, and light carries out incidence from both sides.

[0141] [3] The photoelectric cell of photoelectrical Ikemoto invention connects the optoelectric transducer of the above-mentioned this invention to an external load, and is made to do electric work (power generation). What calls photoelectrochemical cell what the charge transportation material 23 becomes mainly from ion-transport material among photoelectric cells, and makes power generation by sunlight a key objective is called solar battery.

[0142] In order to prevent degradation of a structure and vaporization of contents, as for the side of a photoelectric cell, sealing with polymer, adhesives, etc. is desirable. The external circuit itself connected to a conductive base material and a counter electrode through a lead is easy to be well-known.

[0143] When applying the optoelectric transducer of this invention to a solar battery, the structure inside the cell is the same as the structure of an optoelectric transducer fundamentally mentioned above. Moreover, the solar cell module of this invention containing the optoelectric transducer of this invention can take the same structure as fundamentally as the conventional solar cell module. Generally, a cell is constituted on support substrates, such as a metal and a ceramic, and a solar cell module covers a it top with a restoration resin, cover glass, etc., and takes the structure of incorporating light from the opposite side of a support substrate. It is also possible to consider as the structure of using transparent materials, such as tempered glass, for a support substrate, constituting a cell on it, and incorporating light from the transparent support substrate side. Specifically, the substrate one apparatus module structure used with module structure a super straight type, a substrate type, or potting type, an amorphous-silicon solar cell, etc. is known. Also in the coloring matter sensitization type solar battery using the optoelectric transducer of this invention, module structure can be suitably chosen according to the purpose of use, a service space, and environment. The structure of the solar cell module in this invention which can be used, the desirable mode, etc. are the same as that of a thing given in Japanese Patent Application No. 11-8457.

[0144]

[Example] Hereafter, although an example explains this invention still in detail, this invention is not limited to them.

[0145] 1. With 15g [of titanium-dioxide particles] (product [made from Japanese Aerosil], Degussa P-25), 45g, 1g (Aldrich make, Triton X-100), and a diameter of 0.5mm zirconia-beads

(Nikkato Corp. make) 30g was put into the container made from stainless steel of 200ml of content volume which carried out Teflon (registered trademark) coating of the manufacture inside of titanium-dioxide dispersion liquid, and distributed processing was carried out by 1500rpm for 2 hours using the Sand-grinder mill (product made from eye MEKKUSU). Filtration removed zirconia beads from the obtained dispersion liquid. The mean particle diameter of the titanium-dioxide particle in the obtained dispersion liquid was 2.5 micrometers. In addition, particle size was measured in the master sizer made from MALVERN.

[0146] 2. The glass rod was used and the above-mentioned dispersion liquid were applied to the electric conduction side side of the electrically conductive glass (thing and surface-electrical-resistance about 30ohm/** which carried out cutting processing of the TCO glass [by Asahi Glass Co., Ltd.]-U at the 20mmx20mm size) which has the tin-oxide layer which doped the creation fluorine of TiO2 electrode which adsorbed coloring matter. The coverage of a semiconductor particle was taken as 20 g/m2. At that time, the adhesive tape was stretched to the part by the side of an electric conduction side (from an edge to 3mm), and it considered as the spacer, and glass was put in order and it applied eight sheets at a time at once so that an adhesive tape might come to ends. After the application, it exfoliated and the adhesive tape was air-dried for one day at the room temperature. Next, this glass was put into the electric furnace (muffle furnace FP-32 type made from Yamato Science), it calcinated for 30 minutes at 450 degrees C, and TiO2 electrode was obtained. It flooded with the ethanol solution (3x10-4 mol/l) of coloring matter R-1 for 3 hours, after taking out this electrode and cooling. TiO2 electrode which coloring matter dyed was washed and air-dried by ethanol, after being immersed in the 4-t-butyl pyridine for 15 minutes. The thickness of the obtained photosensitive layer was 6.5 micrometers.

[0147] 3. The acetonitrile solution containing the electrolyte salt MHIm of the photoelectrochemical-cell examples 1-7, the example 1 of comparison, and 20.5 mol/l using the electrolyte constituent containing the production 3-1. solvent of a photoelectrochemical cell (iodine salt of 1-methyl-3-hexyl imidazolium) and 0.05 mol [/l.] iodine was prepared, and the siloxane compound 1-4 was added to this. 10 mass % The siloxane compound made the [solvent + electrolyte salt + siloxane compound] 100 mass %, and used it here. It was made to sink into the crevice which piled up the platinum vacuum evaporationo glass of the coloring matter sensitization TiO2 electrode substrate (20mmx20mm) which produced the obtained solution as mentioned above, and the same size as this using capillarity, introduced into the TiO2 electrode, it closed by the epoxy system encapsulant, and the photoelectrochemical cell of an example 1 using the first electrolyte constituent of this invention was obtained. The photoelectrochemical cell of examples 2-7 using the first electrolyte constituent of this invention was obtained like the above-mentioned example 1 except having changed the solvent and the siloxane compound, as shown in the following table 1. Moreover, except not adding a siloxane compound, the photoelectrochemical cell of the example 1 of comparison was produced like the above-mentioned example 1, and the photoelectrochemical cell of the example 2 of comparison was produced like the above-mentioned example 1 except having changed to the siloxane compound further and having added t-butyl pyridine. The coloring matter used for the photoelectrochemical cell of the above-mentioned examples 1-7 and the examples 1 and 2 of comparison, a siloxane compound and its mass ratio, an electrolyte salt and its concentration, the concentration of iodine, and a solvent are collectively shown in Table 1. In addition, AN in Table 1 expresses an acetonitrile, NMO expresses 3-methyl-2-oxazolidinone, PC expresses propylene carbonate, and MHIm expresses the iodine salt of 1-methyl-3-hexyl imidazolium. Moreover, the mass ratio of a siloxane compound is a mass ratio at the time of making a [solvent + electrolyte salt + siloxane compound] into 100 mass % among Table 1.

[0148]

[Table 1]

光電気化学電池	色素	シロキサン化合物 (質量%)	電解質塩 (mol/l)	ヨウ素 (mol/l)	溶媒
実施例1	R-1	1-4 (10)	MHIm (0.5)	0.05	AN
実施例2	R-1	1-4 (10)	MHIm (0.5)	0.05	NMO
実施例3	R-1	1-4 (10)	MHIm (0.5)	0.05	PC
実施例4	R-1	1-6 (10)	MHIm (0.5)	0.05	AN
実施例5	R-1	1-11 (10)	MHIm (0.5)	0.05	AN
実施例6	R-1	1-13 (10)	MHIm (0.5)	0.05	AN
実施例7	R-1	1-17 (10)	MHIm (0.5)	0.05	AN
比較例1	R-1	なし	MHIm (0.5)	0.05	AN
比較例2	R-1	t-ブチルピリジン (10)	MHIm (0.5)	0.05	AN

[0149] The acetonitrile solution containing the electrolyte salt MHIm of an example 8 - 170.5 mol/l (iodine salt of 1-methyl-3-hexyl imidazolium) and the iodine of 0.05 mol/l was prepared. The siloxane compound 1-4 was added to this solution, the electrophilic agent E-3 was mixed further, and the uniform solution was adjusted. Here, the siloxane compound made the [solvent + electrolyte salt + siloxane compound] 100 mass %, 10 mass % Used it, and it added the electrophilic agent so that the mole ratio of the electrophilic part of the electrophilic agent to the reactive site of a siloxane compound might be set to 1. It was made to sink into the crevice which piled up the platinum vacuum evaporationo glass of the coloring matter sensitization TiO2 electrode substrate (20mmx20mm) which produced the obtained solution as mentioned above, and the same size as this using capillarity, and introduced into the TiO2 electrode. This was left at 50 degrees C for 12 hours, polymerization reaction was performed, it closed by the epoxy system encapsulant, and the photoelectrochemical cell of an example 8 using the second electrolyte constituent of this invention was obtained. The photoelectrochemical cell of examples 9-14 using the second electrolyte constituent of this invention was obtained like the above-mentioned example 8 except having changed a solvent, a siloxane compound, and an electrophilic agent and its mole ratio, as shown in the following table 2. Moreover, it changed to what shows a siloxane compound in Table 2, and the photoelectrochemical cell of examples 15-17 using the second electrolyte constituent of this invention was obtained like the above-mentioned example 8 except having made the amount of the electrophilic agent used into 5 mass % to the siloxane compound. The coloring matter used for the photoelectrochemical cell of the above-mentioned examples 8-17, an electrophilic agent and its mole ratio, a siloxane compound and its mass ratio, an electrolyte salt and its concentration, the concentration of iodine, and a solvent are collectively shown in Table 2. In addition, AN in Table 2 expresses an acetonitrile, NMO expresses 3-methyl-2-oxazolidinone, PC expresses propylene carbonate, and MHIm expresses the iodine salt of 1-methyl-3-hexyl imidazolium. Moreover, among Table 2, the mass ratio of a siloxane compound is a mass ratio at the time of making a [solvent + electrolyte salt + siloxane compound] into 100 mass %, and the mole ratio of an electrophilic agent is a mole ratio of the electrophilic part of the electrophilic agent to the reactive site of a siloxane compound. However, not a mole ratio but the mass ratio (wt%) to a siloxane compound shows the amount of the electrophilic agent used used for the photoelectrochemical cell of examples 15-17.

[0150]

[Table 2]

光電気化学電池	色素	求電子剤 (モル比又は質量比)	シロキサン化合物 (質量%)	電解質塩 (mol/l)	ヨウ素 (mol/l)	溶媒
実施例8	R-1	E-3 (1)	1-4 (10)	MHIm (0.5)	0.05	AN
実施例9	R-1	E-3 (1)	1-4 (10)	MHIm (0.5)	0.05	NMO
実施例10	R-1	E-3 (1)	1-4 (10)	MHIm (0.5)	0.05	PC
実施例11	R-1	E-3 (1)	1-6 (10)	MHIm (0.5)	0.05	AN
実施例12	R-1	E-12 (1)	1-4 (10)	MHIm (0.5)	0.05	AN
実施例13	R-1	E-12 (1)	1-6 (10)	MHIm (0.5)	0.05	AN
実施例14	R-1	E-3 (0.9), E-5 (0.1)	1-4 (10)	MHIm (0.5)	0.05	AN
実施例15	R-1	E-3 (5 wt%)	1-11 (10)	MHIm (0.5)	0.05	AN
実施例16	R-1	E-3 (5 wt%)	1-13 (10)	MHIm (0.5)	0.05	AN
実施例17	R-1	E-3 (5 wt%)	1-17 (10)	MHIm (0.5)	0.05	AN

[0151] The hexa ethylene glycol methacrylic ester ("BUREMMA PE-350" by the Nippon Oil & Fats chemistry company) of 3500mg of examples of comparison, 1g propylene carbonate, and the mixed liquor containing the 2mg polymerization initiator azobisuisobutironitoriru were prepared, and the 500mg iodation lithium was dissolved in this. Next, the vacuum deairing of this mixed liquor was

carried out for 10 minutes, and it applied to the coloring matter sensitization TiO2 electrode substrate (20mmx20mm) produced as mentioned above. Then, after putting under reduced pressure of TiO2 electrode which applied mixed liquor and urging osmosis of a monomer except for the foam in TiO2 electrode, at 60 degrees C, it heated for 1 hour and the polymerization was carried out. It **(ed) for 30 minutes under iodine atmosphere at the room temperature after the polymerization, and iodine was diffused in the obtained polymer. This was piled up with the counter electrode which deposited platinum, and the photoelectrochemical cell (photoelectrochemical cell using the electrolyte the Chemical Society of Japan, 7, and given in 484 page (1997)) of the example 3 of comparison was obtained.

[0152] 3-2. The fused salt A of the photoelectrochemical-cell examples 18-28 and the example 4 of comparison - 660 mass % using the electrolyte constituent containing room temperature fused salt, the fused salt B of 28 mass %, the iodine of 2 mass %, and the siloxane compound 1-4 of 10 mass % were mixed, and the uniform electrolyte constituent was prepared. After applying 5micro of obtained electrolyte constituents l to the coloring matter sensitization TiO2 electrode substrate produced as mentioned above, it put under reduced pressure of this electrode, and the electrolyte constituent was made to permeate. After the electrolyte constituent fully permeated and the air in an electrode fell out, platinum vacuum evaporationo glass was laid on top of this, and the photoelectrochemical cell of an example 18 using the first electrolyte constituent of this invention was obtained. The photoelectrochemical cell of examples 19-28 using the first electrolyte constituent of this invention was obtained like the above-mentioned example 18 except having changed fused salt, its mass ratio, and the siloxane compound, as shown in the following table 3. Moreover, a siloxane compound was not added, but the photoelectrochemical cell of the examples 4 and 5 of comparison was produced like the above-mentioned example 18 except having changed fused salt and its mass ratio, as shown in Table 3, it changed to the siloxane compound further, t-butyl pyridine was added, and the photoelectrochemical cell of the example 6 of comparison was produced like the above-mentioned example 18 except having changed fused salt and its mass ratio, as shown in Table 3. However, the amount of t-butyl pyridine was made into 10 mass %. The coloring matter used for the photoelectrochemical cell of the above-mentioned examples 18-28 and the examples 4-6 of comparison, fused salt and its mass ratio, the mass ratio of iodine, a siloxane compound, and its mass ratio are collectively shown in Table 3. Moreover, the structure of fused salt A-D is shown below.

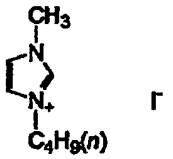
[0153]

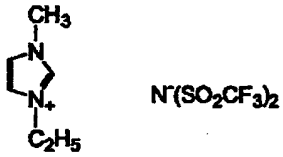
[Table 3]

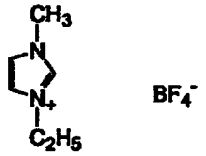
光電気化学電池	色素	溶融塩 (質量%)	ヨウ素 (質量%)	シロキサン化合物 (質量%)
実施例18	R-1	A (60) / B (28)	2	1-4 (10)
実施例19	R-1	A (60) / C (28)	2	1-4 (10)
実施例20	R-1	A (60) / C (28)	2	1-4 (10)
実施例21	R-1	A (60) / B (28)	2	1-6 (10)
実施例22	R-1	D (60) / C (28)	2	1-4 (10)
実施例23	R-1	D (60) / C (28)	2	1-4 (10)
実施例24	R-1	D (60) / C (28)	2	1-6 (10)
実施例25	R-1	D (60) / C (28)	2	1-4 (10)
実施例26	R-1	A (60) / C (28)	2	1-11 (10)
実施例27	R-1	A (60) / C (28)	2	1-13 (10)
実施例28	R-1	A (60) / C (28)	2	1-17 (10)
比較例4	R-1	A (70) / C (28)	2	なし
比較例5	R-1	D (70) / C (28)	2	なし
比較例6	R-1	A (60) / C (28)	2	トブチルピリジン

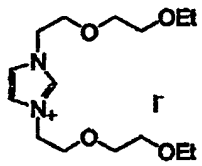
[0154]

[Formula 39]

A 

B 

C 

D 

[0155] The fused salt A of an example 29 - 3960 mass %, the fused salt B of 28 mass %, the iodine of 2 mass %, and the siloxane compound 1-4 of 10 mass % were mixed, the electrophile agent E-3 was added further, and the uniform electrolyte constituent was prepared. Here, the electrophile agent was added so that the mole ratio of the electrophilic part of the electrophile agent to the reactive site of a siloxane compound might be set to 1. After applying 5micro of obtained electrolyte constituents 1 to the coloring matter sensitization TiO2 electrode substrate produced as mentioned above, it put under reduced pressure of this electrode, and the electrolyte constituent was made to permeate. After the electrolyte constituent fully permeated and the air in an electrode fell out, platinum vacuum evaporationo glass was laid on top of this, it was left at 50 degrees C for 10 hours, polymerization reaction was performed, and the photoelectrochemical cell of an example 29 using the second electrolyte constituent of this invention was obtained. The photoelectrochemical cell of examples 30-39 using the second electrolyte constituent of this invention was obtained like the above-mentioned example 29 except having changed fused salt, siloxane compounds and those mass ratios, and an electrophile agent and its mole ratio, as shown in the following table 4. The coloring matter used for the photoelectrochemical cell of the above-mentioned examples 29-39, fused salt and its mass ratio, the mass ratio of iodine, an electrophile agent, its mole ratio, a siloxane compound, and its mass ratio are collectively shown in Table 4. In addition, the mole ratio of an electrophile agent is a mole ratio of the electrophilic part of the electrophile agent to the reactive site of a siloxane compound among Table 4.

[0156]

[Table 4]

光電気化学電池	色素	溶融塩 (質量%)	ヨウ素 (質量%)	求電子剤 (モル比)	シロキサン化合物 (質量%)
実施例29	R-1	A (60) / B (28)	2	E-3 (1)	1-4 (10)
実施例30	R-1	A (60) / C (28)	2	E-3 (1)	1-4 (10)
実施例31	R-1	A (60) / C (28)	2	E-12 (1)	1-4 (10)
実施例32	R-1	A (60) / B (28)	2	E-3 (1)	1-6 (10)
実施例33	R-1	D (60) / C (28)	2	E-3 (1)	1-4 (10)
実施例34	R-1	D (60) / C (28)	2	E-12 (1)	1-4 (10)
実施例35	R-1	D (60) / C (28)	2	E-3 (1)	1-6 (10)
実施例36	R-1	D (60) / C (28)	2	E-3 (0.9), E-5 (0.1)	1-4 (10)
実施例37	R-1	A (60) / C (28)	2	E-3 (1)	1-11 (10)
実施例38	R-1	A (60) / C (28)	2	E-3 (1)	1-13 (10)
実施例39	R-1	A (60) / C (28)	2	E-3 (1)	1-17 (10)

[0157] The photoelectrochemical cell of the example 7 of comparison was produced like the above-mentioned example 3 of comparison except having changed to example of comparison 7 propylene carbonate, and having used the above-mentioned compound C.

[0158] 4. The simulation sunlight which does not include ultraviolet rays was generated by letting AM1.5 filter (product made from Oriel), and a sharp cut filter (Kenko L-42) pass for the light of the xenon lamp of measurement 500W of a photoelectric conversion efficiency (product made from USHIO Electrical and electric equipment). This luminous intensity was 86 mW/cm2. The electrical and electric equipment which irradiated the photoelectrochemical cell of the examples 1-39 produced at 50 degrees C and the examples 1-7 of comparison, and generated this simulation sunlight was measured in the current-potential measuring device (case rhe SMU238 type). The decreasing rate of the short-circuit current density (Jsc) of each photoelectrochemical cell called for by this, an open circuit voltage (Voc), a form factor (FF), a conversion efficiency (eta), and the conversion efficiency after 360-hour continuous irradiation is shown in Tables 5-8.

[0159]

[Table 5]

光電気化学電池	短絡電流密度 (Jsc) mA/cm^2	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (360時間後) %
実施例1	10.1	0.72	0.62	5.24	78
実施例2	9.75	0.72	0.61	4.98	76
実施例3	9.89	0.73	0.62	5.20	77
実施例4	10.2	0.72	0.61	5.21	76
実施例5	9.62	0.73	0.60	4.90	78
実施例6	9.43	0.74	0.61	4.95	78
実施例7	9.67	0.73	0.60	4.92	77
比較例1	9.92	0.85	0.65	4.87	99
比較例2	9.42	0.72	0.61	4.81	99

[0160]

[Table 6]

光電気化学電池	短絡電流密度 (Jsc) mA/cm^2	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (360時間後) %
実施例8	9.12	0.68	0.57	4.11	42
実施例9	8.97	0.67	0.58	3.86	36
実施例10	8.89	0.67	0.56	3.82	35
実施例11	9.10	0.66	0.57	3.98	41
実施例12	9.12	0.68	0.58	4.04	37
実施例13	9.10	0.66	0.56	3.91	33
実施例14	9.11	0.67	0.56	3.97	29
実施例15	7.67	0.68	0.56	3.40	33
実施例16	7.58	0.69	0.57	3.47	35
実施例17	7.90	0.68	0.57	3.56	37
比較例3	2.22	0.64	0.65	1.07	62

[0161]

[Table 7]

光電気化学電池	短絡電流密度 (Jsc) mA/cm^2	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (360時間後) %
実施例18	9.11	0.61	0.57	3.68	18
実施例19	9.08	0.62	0.58	3.80	18
実施例20	9.20	0.62	0.58	3.85	16
実施例21	9.11	0.60	0.58	3.69	17
実施例22	9.28	0.60	0.57	3.69	17
実施例23	9.14	0.60	0.58	3.70	16
実施例24	9.13	0.61	0.57	3.69	16
実施例25	9.09	0.61	0.58	3.74	14
実施例26	8.10	0.62	0.58	3.39	15
実施例27	8.99	0.60	0.57	3.58	16
実施例28	8.98	0.61	0.57	3.63	15
比較例4	7.85	0.52	0.58	2.75	35
比較例5	7.90	0.55	0.59	2.98	30
比較例6	7.20	0.62	0.56	2.91	45

[0162]
[Table 8]

光電気化学電池	短絡電流密度 (Jsc) mA/cm^2	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (360時間後) %
実施例29	8.11	0.57	0.55	2.96	18
実施例30	8.20	0.59	0.55	3.09	18
実施例31	8.20	0.59	0.54	3.03	16
実施例32	8.09	0.56	0.55	2.85	17
実施例33	8.28	0.60	0.55	3.18	17
実施例34	8.28	0.61	0.54	3.17	16
実施例35	8.25	0.58	0.55	3.06	16
実施例36	8.27	0.58	0.54	3.01	14
実施例37	8.01	0.60	0.55	2.64	15
実施例38	7.11	0.61	0.54	2.72	14
実施例39	7.05	0.60	0.54	2.66	15
比較例7	1.40	0.52	0.50	0.42	14

[0163] To this causing [the open circuit voltage] a low photoelectric conversion efficiency low, as for the photoelectrochemical cell of the examples 1, 4, and 5 of comparison, an open circuit voltage is high and the conversion efficiency of the photoelectrochemical cell [the examples 1-7 and the photoelectrochemical cell of 18-28] using the first electrolyte constituent of this invention is improving in connection with it so that more clearly than Table 5 and 7. Moreover, although degradation after dark place preservation is remarkable in the photoelectrochemical cell of the examples 1 and 2 of comparison which contain many organic solvents in an electrolyte constituent, and examples 1-7, by using the first electrolyte constituent of this invention shows that endurance is improved. Moreover, Table 6 and 8 shows that the examples 8-17 and the photoelectrochemical cell of 29-39 using the second electrolyte constituent of this invention show the outstanding conversion efficiency and outstanding endurance as compared with the photoelectrochemical cell of the examples 3 and 7 of comparison using the conventional solid electrolyte.
[0164]
[Effect of the Invention] As explained in full detail above, the first of this invention and second electrolyte constituents are excellent in endurance and charge transportation ability, and the optoelectric transducer and photoelectric cell using this electrolyte constituent show the outstanding endurance and the outstanding photoelectric transfer characteristic. This photoelectric cell is very effective as a solar battery.

[Translation done.]

* NOTICES *

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TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the optoelectric transducer and photoelectric cell in which the endurance and the photoelectric transfer characteristic which were excellent since the electrolyte constituent excellent in endurance and charge transportation ability and this electrolyte constituent were used are shown.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] The liquefied electrolyte constituent (electrolytic solution) which dissolved the electrolyte salt in the solvent has been used from the former as an electrolyte of electrochemical elements, such as a cell, a capacitor, a sensor, a display device, and a record element. However, in the electrochemical element using such a liquefied electrolyte constituent, this constituent may be revealed between prolonged use or preservation, and reliability is missing.
[0003] Although U.S. JP,4927721,B etc. is indicating the optoelectric transducer using the semiconductor particle which carried out sensitization with coloring matter, and the photoelectrochemical cell using this in Nature, the 353rd volume, the 737-740th page, and 1991 Since the liquefied electrolyte constituent is used for the charge transporting bed also in these, this constituent reveals or is drained between prolonged use or preservation, a photoelectric conversion efficiency falls remarkably or there is a case where it stops functioning as an element.
[0004] WO 93/No. 20565 proposed the optoelectric transducer which used the solid electrolyte under such a situation. Moreover, the Chemical Society of Japan, 7, 484 pages (1997) JP,7-288142,A, Solid State Ionics, 89, 263, and (1986) JP,9-27352,A proposed the optoelectric transducer containing the solid electrolyte which used the bridge formation polyethylene-oxide system high molecular compound. However, the optoelectric transducer using these solid electrolytes has the photoelectric transfer characteristic, especially inadequate short-circuit current density, and, in addition, its endurance is not enough, either.
[0005] Moreover, in order to prevent disclosure and an exhaustion of an electrolyte constituent and to raise the endurance of an optoelectric transducer, the method of using a pyridinium salt, an imidazolium salt, a thoria ZORIUMU salt, etc. is indicated (WO 95/No. 18456, JP,8-259543,A, electrochemistry, the 65th volume, No. 11, 923page (1997), etc.). These salts are in a melting state in ordinary temperature (near 25 degree C), and are called room temperature fused salt. Since solvents, such as water and an organic solvent, are unnecessary or little and can be managed with this method, the endurance of a cell improves. However, especially the optoelectric transducer using such room temperature fused salt has a low open circuit voltage, and its photoelectric conversion efficiency is not good.

[Translation done.]

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained in full detail above, the first of this invention and second electrolyte constituents are excellent in endurance and charge transportation ability, and the optoelectric transducer and photoelectric cell using this electrolyte constituent show the outstanding endurance and the outstanding photoelectric transfer characteristic. This photoelectric cell is very effective as a solar battery.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Therefore, the purpose of this invention is offering the optoelectric transducer and photoelectric cell in which the endurance and the photoelectric transfer characteristic which were excellent since the electrolyte constituent excellent in endurance and charge transportation ability and this electrolyte constituent were used are shown.

[Translation done.]

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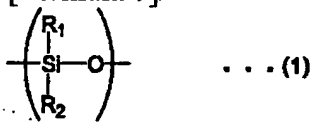
MEANS

[Means for Solving the Problem] The electrolyte constituent containing the polymer which this invention person makes the electrolyte constituent containing a siloxane compound including a specific repeat unit and this siloxane compound react with an electrophile agent wholeheartedly in view of the above-mentioned purpose as a result of research, and is obtained discovered that the outstanding charge transportation ability and outstanding endurance were shown, and hit on an idea of it to this invention.
[0008] namely, the first electrolyte constituent of this invention -- following general formula (1): --
[Formula 7]



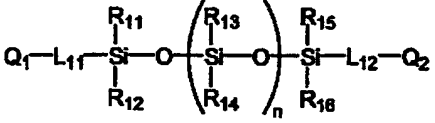
. . . (1)

R_1: L_1-Q_{01}
R_2: L_2-Q_{02}

(However, R1 L1- Q01 (L1 expresses combination or a divalent connection machine)) when Q01 expresses a substituent when L1 expresses combination, and L1 expresses a divalent connection machine, Q01 expresses a hydrogen atom or a substituent Expressing, R2 is L2-Q02 (when Q02 expresses a substituent when L2 expresses combination or a divalent connection machine and L2 expresses combination, and L2 expresses a divalent connection machine, Q02 expresses a hydrogen atom or a substituent.). it expresses It is characterized by containing the siloxane compound which has at least two substituents which react with an electrophile agent and can form covalent bond including the repeat unit expressed.
[0009] Moreover, it is characterized by the second electrolyte constituent of this invention containing the polymer which the electrophile agent which has at least two leaving groups, and the siloxane compound which has at least two substituents which react with an electrophile agent and can form covalent bond including the repeat unit expressed by the above-mentioned general formula (1) are made to react, and is obtained.
[0010] The first of this invention and second electrolyte constituents can be preferably used for a photoelectric cell. The optoelectric transducer of this invention has a conductive layer, a photosensitive layer, a charge transporting bed, and a counter electrode, and it is characterized by this charge transporting bed containing the electrolyte constituent of the above first, or the second electrolyte constituent. The photoelectric cell of this invention uses this optoelectric transducer.
[0011] By filling the following conditions with this invention, the optoelectric transducer and photoelectric cell in which the electrolyte constituent which has further excellent endurance or charge transportation ability, the further excellent endurance, and the photoelectric transfer characteristic are shown are obtained.
[0012] (1) In the first and second electrolyte constituents, as for the substituent which reacts with an electrophile agent and can form covalent bond, it is desirable that it is a basic group, and this basic group is an imidazolyl machine which is not replaced [the pyridyl machine which is not replaced / substitution or /, substitution, or] especially preferably. As for pKa of the conjugate acid of the compound which comes to add hydrogen to this basic group, it is desirable that it is 3-15.

[0013] (2) As for the siloxane compound used for the first and second electrolyte constituents, being expressed by the following general formula (2) is desirable, and being expressed by the following general formula (3) is more desirable.

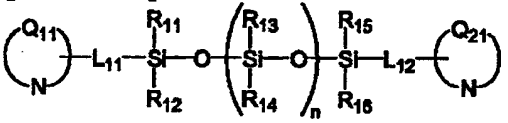
[Formula 8]



. . . (2)

The substituent which Q1 and Q2 react with the above-mentioned electrophile agent independently, respectively, and can form covalent bond is expressed among a general formula (2), R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], respectively, L11 and L12 express a divalent connection machine independently, respectively, and n expresses the integer of 1-1000.

[Formula 9]



. . . (3)

Q11 and Q21 express the atomic group which forms 5 or 6 member ring with a nitrogen atom independently, respectively among a general formula (3), R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or], respectively, L11 and L12 express a divalent connection machine independently, respectively, and n expresses the integer of 1-1000.

[0014] (3) As for Q11 and Q21 in a general formula (3), in the first and second electrolyte constituents, it is desirable respectively to be constituted by one or more sorts of atoms chosen from the group which consists of a carbon atom, a hydrogen atom, a nitrogen atom, an oxygen atom, and a sulfur atom.

[0015] (4) As for 5 or 6 member ring which Q11 and Q21 in a general formula (3) form with a nitrogen atom, respectively, in the first and second electrolyte constituents, it is desirable that they are especially an imidazole ring or a pyridine ring.

[0016] (5) As for pKa of the conjugate acid of the anion which the leaving group which an electrophile agent has ****s and produces, in the second electrolyte constituent, it is desirable that it is ten or less.

[0017] (6) As for the leaving group which an electrophile agent has, in the second electrolyte constituent, it is desirable respectively that they are a halogen atom, an alkylsulfonyloxy machine, or an arylsulfonyloxy machine.

[0018] (7) As for the first and second solvent contents of an electrolyte constituent, it is desirable that it is especially below 10 mass % of the whole electrolyte constituent.

[0019] (8) As for the first and second electrolyte constituents, it is desirable to contain an iodine salt and/or iodine in addition to the above-mentioned siloxane compound and the above-mentioned polymer.

[0020] (9) As for the photosensitive layer of an optoelectric transducer, it is desirable to contain the semiconductor particle by which sensitization was carried out with coloring matter. As for this semiconductor particle, it is desirable that a metal chalcogenide particle is included, and, as for a metal chalcogenide particle, it is desirable that a titanium oxide particle is included. Moreover, as for coloring matter, it is desirable that they are metal complex coloring matter and/or poly methine coloring matter.

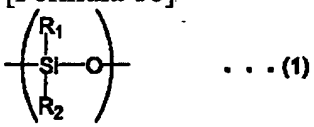
[0021]

[Embodiments of the Invention] [1] The first electrolyte constituent of an electrolyte constituent this invention contains the specific siloxane compound mentioned later. Moreover, the second electrolyte constituent of this invention contains the polymer which this siloxane compound is made to react with the electrophile agent which has at least two leaving groups, and is obtained. The second electrolyte constituent of this invention hardly shows a fluidity, but is excellent in endurance and

charge transportation ability. The first of this invention and second electrolyte constituents may contain an electrolyte salt, a solvent, etc. further. Hereafter, each the first of this invention and second components of an electrolyte constituent are explained in full detail.

[0022] (A) The siloxane compound used for the first of a siloxane compound this invention and second electrolyte constituents has at least two substituents which react with an electrophile agent and can form covalent bond, including the repeat unit expressed by the following general formula (1). In the second electrolyte constituent of this invention, this siloxane compound receives ornamentation of alkylation, class[the / 4th]-izing, etc. by the electrophile agent.

[Formula 10]



. . . (1)

R_1: L_1-Q_{01}

R_2: L_2-Q_{02}

[0023] R1 expresses L1-Q01 among a general formula (1), and R2 expresses L2-Q02. Here, when Q01 expresses a substituent when L1 expresses combination or a divalent connection machine and L1 expresses combination, and L1 expresses a divalent connection machine, Q01 expresses a hydrogen atom or a substituent. Moreover, when Q02 expresses a substituent when L2 expresses combination or a divalent connection machine and L2 expresses combination, and L2 expresses a divalent connection machine, Q02 expresses a hydrogen atom or a substituent. when they may also be included although a siloxane compound includes one repeat unit expressed by the general formula (1), and more than one are included, even if R1 and R2 in each repeat unit are the same respectively, they may differ [two or more].

[0024] When L1 or L2 expresses a divalent connection machine, as the example An alkylene machine, An alkenylene group, an arylene machine, -O-, -S-, -CO-, -NR'- (R' is a hydrogen atom or an alkyl group), - SO2- and - SiR" -- R'"- (R -- "and R'" -- Respectively -- Alkyl Group --) An aryl group, an alkoxy group or aryloxy groups, such combination, etc. are mentioned. Especially -(CH2) m1-, -O-, -(OCH2CH2) m1-, - M1-O-, -(OCH2CH2) M1-CH2-, (OCH2CH2) - (OCH2CH2CH2) m1-, -(OCH2CH2CH2) m1-O-, -(OCH2CH2CH2) m1-CH2-, -(CH2) m1-(Si(CH3)2-O) m2-, and -O-(CH2) m1-(Si(CH3)2-O) m2- is desirable. In addition, m1 and m2 express the integer of 1-20, respectively.

[0025] the case where Q01 and Q02 express a substituent -- as the example of a desirable substituent -- an alkyl group (the shape of a straight chain --) You may be a letter of branching, or annular. For example, a methyl group, an ethyl group, n-propyl group, An isopropyl machine, t-butyl, n-octyl machine, a ray KOSHIRU machine, 2-chloro ethyl group, 2-cyano ethyl group, a 2-ethylhexyl machine, a cyclohexyl machine, a cyclopentylic group, aryl groups (for example, a phenyl group --), such as a 4-n-dodecyl cyclohexyl machine Heterocycle machines, such as p-tolyl group, a naphthyl group, and m-chlorophenyl machine (it is the univalent basis which comes preferably to remove one hydrogen atom from the aromatic heterocycle compound or un-aromatic heterocycle compound which is not replaced [the substitution of 5 or 6 members, or]) For example, 2-furil machine, 2-thienyl group, 2-pyrimidinyl group, 2-pyridyl machine, halogen atoms (for example, a chlorine atom --), such as 4-pyridyl machine and 1-imidazolyl machine a cyano group, a nitro group and hydroxyl groups, such as a bromine atom and an iodine atom, and an alkoxy group (for example, a methoxy machine --) An ethoxy basis, an isopropoxy group, a t-butoxy machine, n-octyloxy machine, a 2-methoxyethoxy machine, -O(CH2CH2O) mCH3 grade, and a silyloxy machine (for example, a trimethyl silyloxy machine --) t-buthyldimethyl silyloxy machine, a trimethoxy silyloxy machine, etc.; an acyloxy machine (for example, a formyloxy machine, an acetyloxy machine, and a pivaloyloxy machine --) A stearoyl oxy-basis, a benzoyloxy machine, p-methoxypheny carbonyloxy group, etc., a carbamoyloxy machine (for example, N and an N-dimethylcarbamoyloxy machine --) A N,N-diethylcarbamoyloxy machine, morpholino carbonyloxy group, An N and N-G n-octyl aminocarbonyl oxy-basis, an N-n-octyl carbamoyloxy machine, etc., alkoxy carbonyloxy group (for example, a

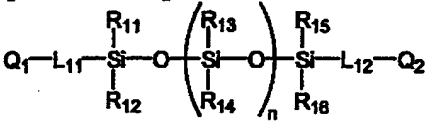
methoxycarbonyloxy machine --) An ethoxycarbonyloxy machine, t-buthoxycarbonyloxy machine, n-octyl carbonyloxy group, etc., aryloxy carbonyloxy group (for example, a phenoxy carbonyloxy machine --) p-methoxy phenoxy carbonyloxy machine, an p-n-hexadecyl oxy-phenoxy carbonyloxy machine, etc., the amino group (for example, the amino group, a methylamino machine, a dimethylamino machine, and the Ernie Reno machine --) the acylamino machines (for example, a formylamino machine --), such as N-methyl ANIRINO machine and a diphenylamino machine An acetylamino machine, the pivaloyl amino group, the lauroyl amino group, a benzoylamino machine, 3, 4, a 5-tree n-octyloxy phenyl carbonylamino machine, etc., the aminocarbonyl amino group (for example, carbamoyl amino machine, N, and N-dimethylamino carbonylamino machine --) N and N-diethylamino carbonylamino machine, a morpholino carbonylamino machine, etc., an alkoxycarbonylamino machine (for example, a methoxycarbonylamino machine --) An ethoxycarbonylamino machine, t-butoxycarbonylamino machine, n-octadecyloxycarbonylamino machine, aryloxycarbonylamine machines (for example, a phenoxycarbonylamino machine --), such as N-methyl methoxycarbonylamino machine p-chloro phenoxycarbonylamino machine, an m-n-octyloxy phenoxycarbonylamino machine, etc., a sulfamoylamino group (for example, sulfamoylamino group, N, and N-dimethylamino sulfonylamino machine --) alkyl sulfonylamino machines (for example, a methylsulfonylamino machine --), such as an N-n-octyl amino sulfonylamino machine aryl sulfonylamino machines (for example, a phenyl sulfonylamino machine --), such as a butylsulphonylamino machine 2, 3, 5-TORIKURORO phenyl sulfonylamino machine, p-methylphenyl sulfonylamino machine, etc., a sulfhydryl group and an alkyl thio machine (for example, a methylthio machine and an ethyl thio machine --) aryl thio machines (for example, a phenylthio machine --), such as an n-hexadecyl thio machine heterocycle thio machines (for example, a 2-benzothiazolethio group --), such as p-chloro phenylthio machine and m-methoxy phenylthio machine sulfamoyl groups (for example, N-ethyl sulfamoyl group --), such as a 1-phenyl tetrazole-5-IRUCHIO machine N-(3-dodecyloxy propyl) sulfamoyl group, N, and N-dimethyl sulfamoyl group, N-acetyl sulfamoyl group, N-benzoyl sulfamoyl group, alkyl sulfinyl machines (for example, a methyl sulfinyl machine --), such as N-(N'-phenylcarbamoyl) sulfamoyl group aryl sulfinyl machines (for example, a phenyl sulfinyl machine --), such as an ethyl sulfinyl machine alkyl sulfonyl machines (for example, a methyl sulfonyl machine --), such as p-methylphenyl sulfinyl machine aryl sulfonyl machines (for example, a phenyl sulfonyl machine --), such as an ethyl sulfonyl machine acyl groups (for example, an acetyl group --), such as p-methylphenyl sulfonyl machine A pivaloyl machine, 2-chloro acetyl group, a stearoyl machine, a benzoyl, aryloxy carbonyl groups (for example, a phenoxy carbonyl group --), such as an p-n-octyloxy phenyl carbonyl group o-chloro phenoxy carbonyl group, m-nitroglycerine phenoxy carbonyl group, alkoxy carbonyl groups (for example, a methoxycarbonyl group --), such as a p-t-butyl phenoxy carbonyl group An ethoxycarbonyl machine, a t-butoxycarbonyl machine, n-octadecyl oxycarbonyl machine, etc., a carbamoyl group (for example, a carbamoyl group and N-methyl carbamoyl group --) An N and N-dimethyl carbamoyl-group, N, and N-G n-octyl carbamoyl group, Silyl machines, such as N-(methyl sulfonyl) carbamoyl group (it is the silyl machine which is not replaced [the substitution of carbon numbers 3-30, or] preferably) For example, a trimethylsilyl machine, t-butyldimethylsilyl machine, a phenyl dimethylsilyl machine, etc., Phosphino machines (being the phosphino machine which is not replaced [the substitution of carbon numbers 2-30 or] preferably for example, a dimethyl phosphino machine, a diphenyl phosphino machine, a methylphenoxy phosphino machine, etc.) etc. are mentioned. Especially, an alkyl group, an aryl group, a silyl machine, an alkoxy group, an aryloxy group, a silyloxy machine, a heterocycle machine, the amino group, an alkyl thio machine, and a phosphino machine are more desirable, and an alkyl group, a silyl machine, an alkoxy group, a silyloxy machine, and especially a heterocycle machine are desirable.

[0026] The above-mentioned siloxane compound has two or more substituents which react with an electrophilic agent and can form covalent bond. As for the substituent which reacts with an electrophilic agent and can form covalent bond, in the first and second electrolyte constituents, it is desirable that it is a basic group. pKa of the conjugate acid of the compound with which a basic group comes to add hydrogen to it points out three or more bases here. As for pKa of this conjugate acid, it is desirable that it is 3-15, and it is more desirable that it is 4-12. such a basic group -- the amino

group (a dimethylamino machine and a diethylamino machine --) nitrogen-containing heterocycle machines (a morpholino machine and a quinuclidinyl machine --), such as the Ernie Reno machine A piperazinyl machine, a piperidino machine, a pyrrolidino machine, an imidazolyl machine, 2-methyl imidazolyl machine, A quinolyl machine, an acridinyl machine, a pyridyl machine, 2-methyl pyridyl machine, It is desirable that they are guanidino machines (trimethyl guanidino machine etc.), such as a diazabicyclo undecenyl machine, it is more desirable that it is a nitrogen-containing heterocycle machine, and it is desirable that it is especially the imidazolyl machine which is not replaced [the pyridyl machine which is not replaced / substitution or /, substitution, or]. The above-mentioned siloxane compound may have such a basic group at the side chain and/or end in the repeat unit expressed by the general formula (1). When it has this basic group in the side chain in the repeat unit expressed by the general formula (1), Q01 in a general formula (1) and/or Q02 are these basic groups.

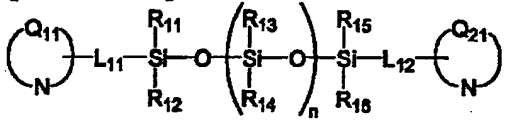
[0027] As for the siloxane compound used for the first of this invention, and second electrolyte constituents, being expressed by the following general formula (2) is desirable, and being expressed by the following general formula (3) is more desirable.

[Formula 11]



. . . (2)

[Formula 12]



. . . (3)

[0028] Q1 and Q2 express the substituent which reacts with an electrophile agent independently, respectively and can form covalent bond among a general formula (2). The electrophile agent in this substituent and the atom which reacts are a nitrogen atom, the Lynn atom, or a sulfur atom preferably, is a nitrogen atom or the Lynn atom more preferably, and is a nitrogen atom especially preferably. As a substituent which Q1 and Q2 express, the amino group, a phosphino machine, a heterocycle machine, an alkyl thio machine, etc. are mentioned.

[0029] R11-R16 express independently the aryl group which is not replaced [the alkyl group which is not replaced / substitution or /, substitution, or] among a general formula (2), respectively. R11-R16 are the alkyl groups of carbon numbers 1-10 preferably, are the alkyl group of carbon numbers 1-3 more preferably, and are a methyl group especially preferably.

[0030] The above Q1 and Q2, and R11-R16 may have the substituent, respectively. as the desirable example of this substituent -- an alkyl group (a methyl group and an ethyl group --) A propyl group, an isopropyl machine, a butyl, a pentyl machine, a hexyl machine, An octyl machine, a 2-ethylhexyl machine, t-octyl machine, a decyl group, the dodecyl, A tetradecyl machine, 2-hexyl decyl group, an octadecyl machine, a cyclohexyl machine, alkenyl machines (a vinyl group --), such as a cyclopentylic group, 2-carboxy ethyl group, and a benzyl A halogens atom, such as an allyl group (a fluorine atom, a chlorine atom, a bromine atom, iodine atom, etc.), A cyano group, an alkoxy group (a methoxy machine, an ethoxy basis, methoxyethoxy machine, etc.), aryloxy machines (phenoxy machine etc.) and an alkyl thio machine (a methylthio machine --) Acyl groups, such as an ethyl thio machine (an acetyl group, a propionyl machine, benzoyl, etc.), sulfonyl machines (a methane sulfonyl machine, benzenesulphonyl machine, etc.) and an acyloxy machine (an acetoxy machine --) sulfonyloxy machines (a methane sulfo NIRIOKISHI machine --), such as a benzoyloxy machine Phosphonyl groups, such as a toluenesulfonyloxy machine (diethyl phosphonyl group etc.), Amide groups (an acetylamino machine, benzoylamino machine, etc.), carbamoyl groups (N and N-dimethyl carbamoyl group, N-phenylcarbamoyl machine, etc.), an aryl group, heterocycle machines (a phenyl group, toluyl machine, etc.) (a pyridyl machine, an imidazolyl machine, furanyl machine, etc.), etc. are mentioned.

[0031] L11 and L12 express a divalent connection machine independently among a general formula

(2), respectively. As an example of this divalent connection machine, the connection machine which comes to combine an alkylene machine, an alkenylene group, an arylene machine, -O-, -S-, -CO-, -NR'- (for R' to express a hydrogen atom or an alkyl group), -SO2-, -SiRR'- (for R and R' to express an alkyl group or an aryl group, respectively), and these [two / or more] is mentioned.

[0032] When L11 and L12 are an alkylene machine, an alkenylene group, or an arylene machine, These A halogen atom (a fluorine atom, a chlorine atom, a bromine atom, iodine atom, etc.), A hydroxyl group, the amino group, a nitro group, a carboxyl group, a carbamoyl group, a sulfonic group, A sulfonamide machine, acyl groups (a formyl machine, acetyl group, etc.), an acyloxy machine, The acylamino machine, alkyl groups (an acetamino machine, bends amino group, etc.), You may have substituents, such as alkoxy groups (a methoxy machine, an ethoxy basis, methoxyethoxy machine, etc.), an AKOKISHI carbonyl group, an alkyl sulfonyl machine, an aryl group, an aryloxy group, and aryl sulfonyl machines (phenoxy machine etc.).

[0033] n expresses the integer of 1-1000 among a general formula (2). n is the integer of 1-500 preferably, and is the integer of 1-100 especially preferably. If n is larger than 1000, a reactant fall with ionic conductivity and an electrophile agent will be caused.

[0034] Q11 and Q21 express the atomic group which forms 5 or 6 member ring with a nitrogen atom independently, respectively among a general formula (3). As for Q11 and Q21, it is desirable to be constituted by one or more sorts of atoms chosen from the group which consists of a carbon atom, a hydrogen atom, a nitrogen atom, an oxygen atom, and a sulfur atom.

[0035] As for 5 or 6 member ring formed of Q11 and Q21, it is desirable that it is an unsaturation ring. As 5 member rings, a pyrrolidine ring, an oxazole ring, a thiazole ring, an imidazole ring, a pyrazole ring, an isoxazole ring, a thiadiazole ring, an oxadiazole ring, and a triazole ring are desirable, a thiazole ring, an imidazole ring, and a triazole ring are more desirable, and especially an imidazole ring is desirable. As 6 member rings, a morpholine ring, a piperidine ring, a pyridine ring, a pyrimidine ring, a pyridazine ring, a pyrazine ring, and a triazine ring are desirable, and especially a pyridine ring is desirable.

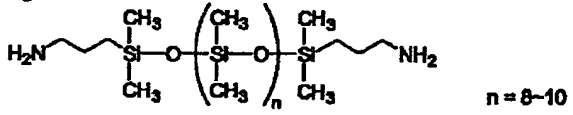
[0036] R11-R16, L11 and L12, and n in a general formula (3) are them in a general formula (2), and homonymy, and its same is said of a desirable mode.

[0037] Although the example 1-1 to 1-18 of the siloxane compound used for the first of this invention and second electrolyte constituents is shown below, this invention is not limited to them.

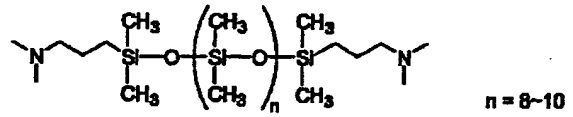
[0038]

[Formula 13]

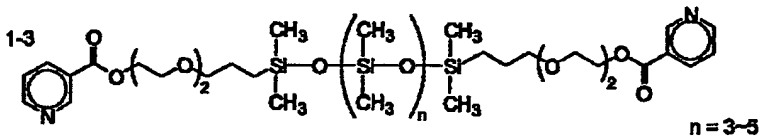
1-1



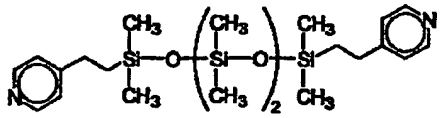
1-2



1-3

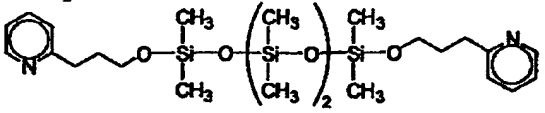


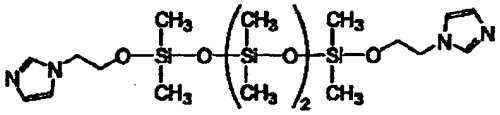
1-4

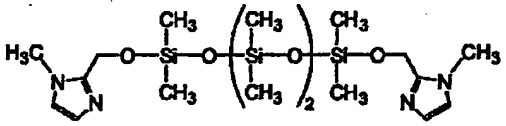


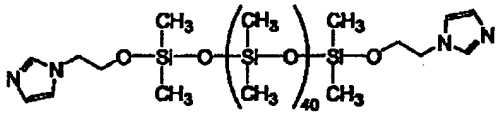
[0039]

[Formula 14]

1-5 

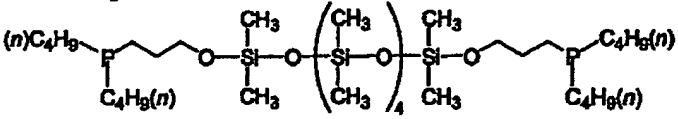
1-6 

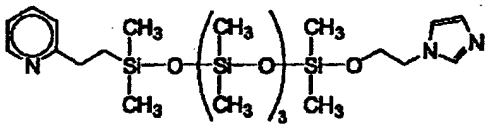
1-7 

1-8 

[0040]

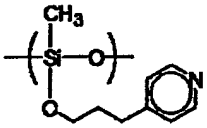
[Formula 15]

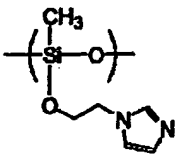
1-9 

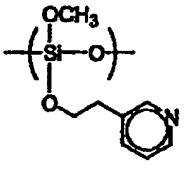
1-10 

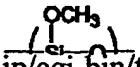
[0041]

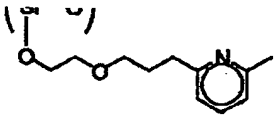
[Formula 16]

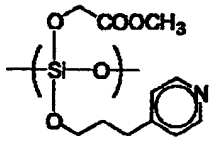
1-11 

1-12 

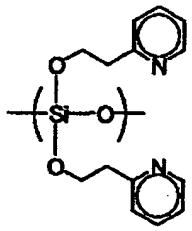
1-13 

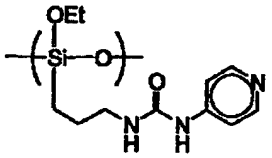


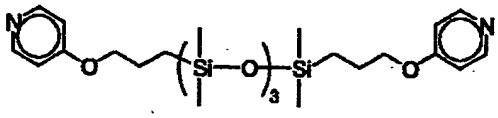
1-14 

1-15 

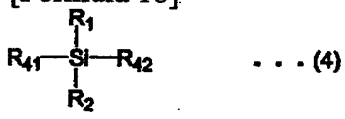
[0042]
[Formula 17]

1-16 

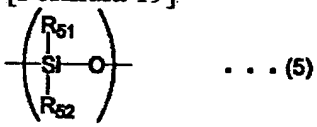
1-17 

1-18 

[0043] The siloxane compound used by this invention is easily compoundable with the substitution reaction by R1-H of a compound and/or R2-H which are expressed by the polymerization of the silane compound expressed by the following general formula (4), and the following general formula (5), the high DOROSHI relation reaction of the compound and olefin compound which are expressed by the following general formula (6), the condensation reaction of the compound and the alcoholic compound which are expressed by the following general formula (7), etc.
[0044]
[Formula 18]

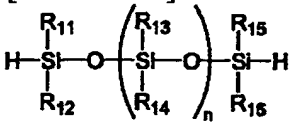
 . . . (4)

R41 and R42 express a halogen atom or an alkoxy group independently among a general formula (4), respectively.
[0045]
[Formula 19]

 . . . (5)

R51 and R52 express an alkoxy group or an aryloxy group independently among a general formula (5), respectively.
[0046]

[Formula 20]

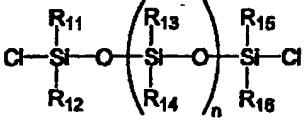


. . . (6)

R11-R16 and n in a general formula (6) are them in a general formula (2), and homonymy, and its same is said of a desirable mode.

[0047]

[Formula 21]



. . . (7)

R11-R16 and n in a general formula (7) are them in a general formula (2), and homonymy, and its same is said of a desirable mode.

[0048] (B) The electrophilic agent used for the second electrolyte constituent of an electrophilic agent this invention has at least two leaving groups. This electrophilic agent reacts with "the substituent which reacts with an electrophilic agent and can form covalent bond" which the above-mentioned siloxane compound has, and when alkylation, onium chlorination, the 4th class-ization, etc. carry out this substituent, it forms the shape of a straight line, and the polymer over which the bridge was constructed.

[0049] In order to make moderate the degree of cross linking of the polymer which the above-mentioned siloxane compound and an electrophilic agent are made to react, and is obtained, as for the number of leaving groups, it is desirable that they are 2-4 pieces, and it is desirable that they are especially two pieces. If there are many leaving groups, a degree of cross linking will become high, consequently membraneous quality becomes hard, and ionic conductivity falls. Moreover, as for pKa of the conjugate acid of the anion which a leaving group ****s and produces, it is desirable that it is ten or less, and it is more desirable that it is five or less.

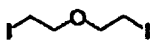
[0050] Leaving groups may be a halogen atom, an alkylsulfonyloxy machine, an arylsulfonyloxy machine, an acyloxy machine, etc., respectively. A halogen atom, an alkylsulfonyloxy machine, and an arylsulfonyloxy machine are desirable especially. As a halogen atom, an iodine atom, a bromine atom, and a chlorine atom are desirable, and an iodine atom and a bromine atom are more desirable. As an alkylsulfonyloxy machine, a methyl sulfonyloxy machine, a chloro methyl sulfonyloxy machine, and perfluoroalkyl sulfonyloxy machines (trifluoromethyl sulfonyloxy machine etc.) are desirable. As an arylsulfonyloxy machine, a benzene sulfonyloxy machine, a p-toluenesulfonyloxy machine, p-chlorobenzene sulfonyloxy machine, and p-nitrobenzene sulfonyloxy machine are desirable. As an acyloxy machine, the alkylcarbonyloxy machines (trifluoromethyl carbonyloxy group etc.) and aryl-carbonyloxy groups (p-fluoro phenyl carbonyloxy group etc.) which carried out fluorine substitution of all or a part of hydrogen atoms are desirable.

[0051] The amount of the electrophilic agent used can be arbitrarily defined according to the molecular weight or the degree of cross linking of a reaction rate with the above-mentioned siloxane compound, or the polymer to generate. The 0.01-2Eq of the 0.05-1.5Eq of the amount of the electrophilic agent used is 0.1-1Eq especially preferably more preferably preferably to the number of mols of "the substituent which reacts with an electrophilic agent and can form covalent bond" which a siloxane compound has. When the number of mols of the substituent which reacts with the electrophilic agent which a siloxane compound has, and can form covalent bond is not clear, the mass ratio of the electrophilic agent to the mass of a siloxane compound is one to 100 mass % preferably, and is three to 70 mass % more preferably. Even if it uses an electrophilic agent independently, it may use two or more sorts together. Although this invention shows the example E-1 to E-27 of an usable electrophilic agent hereafter, this invention is not limited to them.

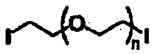
[0052]

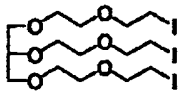
[Formula 22]

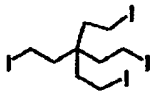
E-1 

E-2 

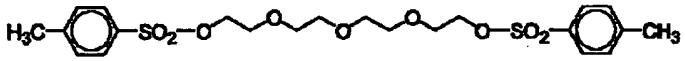
E-3 

E-4  n=8

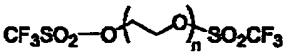
E-5 

E-6 

E-7 

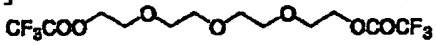
E-8 

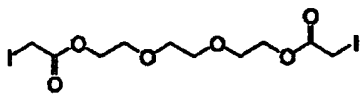
E-9  n=8

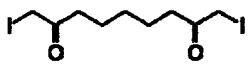
E-10  n=8

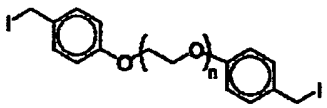
[0053]

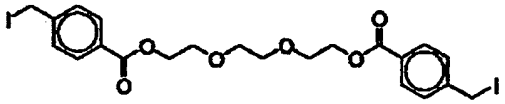
[Formula 23]

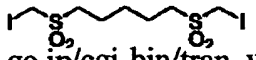
E-11 

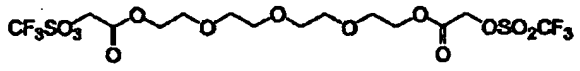
E-12 

E-13 

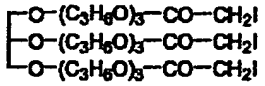
E-14 

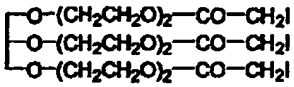
E-15 

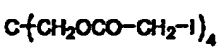
E-16 

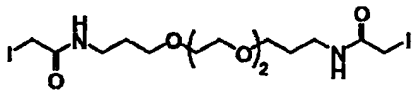
E-17 

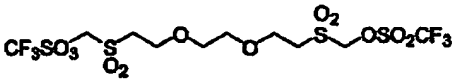
[0054]
[Formula 24]

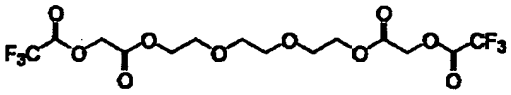
E-18 

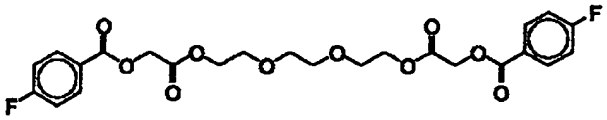
E-19 

E-20 

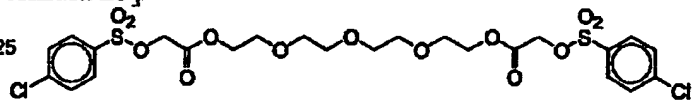
E-21 

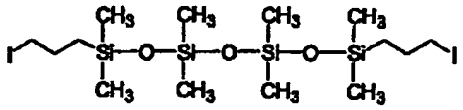
E-22 

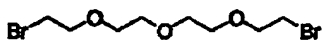
E-23 

E-24 

[0055]
[Formula 25]

E-25 

E-26 

E-27 

[0056] (C) The polymer used for the second electrolyte constituent of a polymerization-reaction this invention can be obtained by the polymerization reaction of the above-mentioned electrophilic agent and a siloxane compound. The polymerization of them is carried out by the alkylation reaction which occurs in detail between the electrophilic part in an electrophilic agent, and the substituent which reacts with this electrophilic agent in a siloxane compound, and can form covalent bond, the reaction (for example, the 4th class-ized reaction of nitrogen) which forms an onium salt. As for the mass average molecular weight of the polymer obtained, it is desirable that it is 1000-1 million, and it is more desirable that it is 2000-500,000.

[0057] As for polymerization reaction, it is desirable to carry out besides an electrophilic agent and a siloxane compound under the conditions with which the electrolyte salt mentioned later coexists.

Although an electrolyte salt may be added after a reaction, it is difficult to distribute an electrolyte salt uniformly in a polymer in this case, and it is not desirable.

[0058] When preparing the reaction solution containing a siloxane compound, an electrophilic agent, and an electrolyte salt and performing polymerization reaction, when a [siloxane compound + electrolyte salt + solvent] is made into 100 mass %, as for the mass ratio of a siloxane compound, it is desirable to consider as 1 - 50 mass %, and it is more desirable to consider as 3 - 30 mass %. Since carrier mobility will fall if a fluidity becomes that a siloxane compound is under 1 mass % inadequate and 60 mass % is exceeded, it is not desirable. In addition, even if it uses a siloxane compound independently, it may use two or more sorts together.

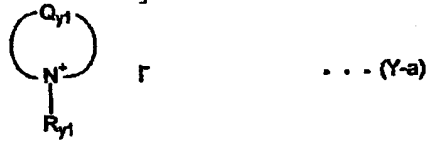
[0059] (D) As an electrolyte salt electrolyte salt, they are (a) I2 and an iodide (it LiI(s)), for example. NaI, KI, CsI, the metal iodide of CaI2 grade, tetrapod alkylammonium iodide, Combination with the 4th class ammonium iodine salts, such as pyridinium iodide and imidazolium iodide, etc., (b) -- Br2 and a bromide (LiBr, NaBr, KBr, CsBr, and the metal bromide of CaBr2 grade --) Combination with the 4th class ammonium bromine salts, such as a tetrapod alkylammonium star's picture and a pyridinium star's picture, etc., (c) Metal complexes (a ferrocyanic-acid salt-ferricyanic-acid salt, ferrocene-ferricinium ion, etc.), (d) sulfur compounds (the poly sodium sulfide, alkyl thiol-alkyl disulfide, etc.), (e) viologen coloring matter, a hydroquinone-quinone, etc. can be used. Especially, the combination of I2 and the 4th class ammonium iodine salt is desirable. You may mix and use an electrolyte salt.

[0060] Moreover, EP718288, WO 95/18456, J.Electrochem.Soc., Vol.143, No.10, and 3099 (1996), as an electrolyte salt Inorg.Chem., 35, and 1168-1178 (1996), JP,8-259543,A, electrochemistry, the 65th volume, No. 11, and 923 pages (1997) etc. -- fused salt, such as a pyridinium salt indicated, an imidazolium salt, and a thoria ZORIUMU salt, can also be used The quality of molten salt electrolysis is desirable especially from a viewpoint of coexistence of endurance and charge transportation ability. In addition, fused salt here is liquefied in a room temperature, or it is the salt of the low melting point and it is [as for the melting point, it is desirable that it is 100 degrees C or less, and] desirable [the melting point] that it is especially near a room temperature.

[0061] as the fused salt which can be preferably used by this invention -- the following general formula (Y-a) -- what is expressed by either is mentioned for and (Y-b) (Y-c)

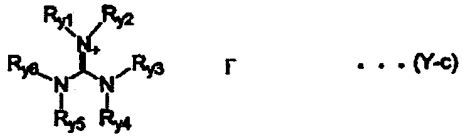
[0062]

[Formula 26]



. . . (Y-a)

. . . (Y-b)



. . . (Y-c)

[0063] Qy1 expresses the atomic group which forms the aromatic cation of 5 or 6 member ring with a nitrogen atom among a general formula (Y-a). As for Qy1, it is desirable to be constituted by one or more sorts of atoms chosen from the group which consists of a carbon atom, a hydrogen atom, a nitrogen atom, an oxygen atom, and a sulfur atom.

[0064] It is desirable that they are an oxazole ring, a thiazole ring, an imidazole ring, a pyrazole ring,

an isoxazole ring, a thiadiazole ring, an oxadiazole ring, a triazole ring, the Indore ring, or a pyrrole ring, as for 5 member rings formed of Qy1, it is more desirable that they are an oxazole ring, a thiazole ring, or an imidazole ring, and it is desirable that they are especially an oxazole ring or an imidazole ring. As for 6 member rings formed of Qy1, it is desirable that they are a pyridine ring, a pyrimidine ring, a pyridazine ring, a pyrazine ring, or a triazine ring, and it is more desirable that it is a pyridine ring.

[0065] Ay1 expresses a nitrogen atom or the Lynn atom among a general formula (Y-b).

[0066] A general formula (Y-a), and (Y-b) (Y-c) inner Ry1-inner Ry6 are an alkyl group (even if it has the shape of the carbon atomic numbers 1-24 and a straight chain preferably and is a letter of branching) which is not replaced [substitution or] independently, respectively. You may be a ring type. Moreover, for example, a methyl group, an ethyl group, a propyl group, An isopropyl machine, a pentyl machine, a hexyl machine, an octyl machine, a 2-ethylhexyl machine, t-octyl machine, a decyl group, a dodecyl machine, a tetradecyl machine, 2-hexyl decyl group, ARUKENIRU machines which are not replaced [substitution or], such as an octadecyl machine, a cyclohexyl machine, and a cyclopentylic group (even if it has the shape of the carbon atomic numbers 2-24 and a straight chain preferably, you may be a letter of branching) For example, a vinyl group, an allyl group, etc. are expressed, and it is the alkyl group of the carbon atomic numbers 2-18, or the ARUKENIRU machine of the carbon atomic numbers 2-18 more preferably, and is the alkyl group of the carbon atomic numbers 2-6 especially preferably.

[0067] Moreover, among Ry1-Ry4 in a general formula (Y-b), the un-aromatic ring in which two or more connect with mutually and they contain Ay1 may be formed, two or more may connect mutually and they may form a ring structure among Ry1-Ry6 in a general formula (Y-c).

[0068] A general formula (Y-a), inner Qy1, and Ry1-Ry6 may have the substituent. as the desirable example of this substituent -- a halogen atom (it Cl(s) and Br(s) F --) cyano groups, such as I, and an alkoxy group (a methoxy machine, an ethoxy basis, and a methoxyethoxy machine --) Aryloxy machines (phenoxy machine etc.), such as a methoxyethoxy ethoxy basis, Alkyl thio machines (a methylthio machine, ethyl thio machine, etc.), an alkoxy carbonyl group (ethoxycarbonyl machine etc.), carbonate machines (ethoxycarbonyloxy machine etc.) and an acyl group (an acetyl group --) sulfonyl machines (a methane sulfonyl machine --), such as a propionyl machine and a benzoyl Acyloxy machines (an acetoxy machine, benzoyloxy machine, etc.), such as a benzenesulphonyl machine, A sulfonyloxy machine (a methane sulfonyloxy machine, toluenesulfonyloxy machine, etc.), phosphonyl groups (diethyl phosphonyl group etc.) and an amide group (an acetylamino machine --) Carbamoyl groups, such as a benzoylamino machine (N and N-dimethyl carbamoyl group etc.), an alkyl group (a methyl group, an ethyl group, a propyl group, an isopropyl machine, and a cyclo propyl group --) Aryl groups, such as a butyl, 2-carboxy ethyl group, and a benzyl, heterocycle machines (a phenyl group, toluyl machine, etc.) (a pyridyl machine, an imidazolyl machine, furanyl machine, etc.), ARUKENIRU machines (a vinyl group, 1-propenyl machine, etc.), a silyl machine, a silyloxy machine, etc. are mentioned.

[0069] The fused salt expressed by the above-mentioned general formula (Y-a) - (Y-c) either may form a polymer through either Qy1, and Ry1-Ry6.

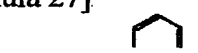
[0070] You may use the fused salt expressed by the above-mentioned general formula (Y-a) - (Y-c) either, mixing with the salt which could use it, having mixed two or more sorts even if it used it independently, and replaced iodide ion I- by other anions. As an anion which replaces I-, halogenide ion, SCN- (Cl-, Br-, etc.), BF4-, PF6-, ClO4-, 2 (CF3SO2)N-, 2 (CF3CF2SO2)N-, CF3SO3-, CH3SO3-, CF3COO-, Ph4B-, 3(CF3SO2) C-, etc. are desirable. They are SCN-, BF4-, CF3SO3-, CF3COO-, or (CF3SO2) 2N- more preferably.

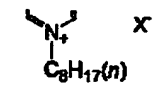
[0071] Moreover, alkali-metal salts, such as other iodine salts and CF3COOLi like LiI, CF3COONa, LiSCN, and NaSCN, can also be added. As for the addition of an alkali-metal salt, it is desirable to consider as a 0.02 - 2 mass % grade, and it is still more desirable to consider as 0.1 to 1 mass %.

[0072] Although - (Y29) is listed to the example (Y1) of the electrolyte salt preferably used by this invention, and the following, they do not limit this invention.

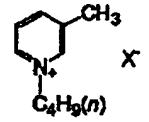
[0073]

[Formula 27]

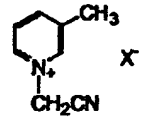


(Y1) 

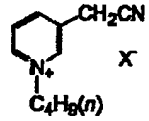
Y1-2 : X⁻=BF_4^-
Y1-3 : X⁻=$N^-(SO_2CF_3)_2$
Y1-4 : X⁻=PF_6^-

(Y2) 

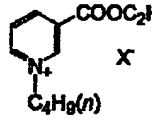
Y2-1 : X⁻=I^-
Y2-2 : X⁻=BF_4^-
Y2-3 : X⁻=$N^-(SO_2CF_3)_2$
Y2-4 : X⁻=CF_3COO^-
Y2-5 : X⁻=SCN^-
Y2-6 : X⁻=$CF_3SO_3^-$

(Y3) 

Y3-1 : X⁻=I^-
Y3-2 : X⁻=BF_4^-
Y3-3 : X⁻=$N^-(SO_2CF_3)_2$

(Y4) 

Y4-1 : X⁻=I^-
Y4-2 : X⁻=BF_4^-
Y4-3 : X⁻=$N^-(SO_2CF_3)_2$

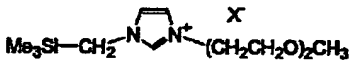
(Y5) 

Y5-1 : X⁻=I^-
Y5-2 : X⁻=BF_4^-
Y5-3 : X⁻=$N^-(SO_2CF_3)_2$

(Y6) 

Y6-1 : X⁻=I^-
Y6-2 : X⁻=BF_4^-
Y6-3 : X⁻=$N^-(SO_2CF_3)_2$
Y6-4 : X⁻=Br^-
Y6-5 : X⁻=CF_3COO^-
Y6-6 : X⁻=SCN^-
Y6-7 : X⁻=$CF_3SO_3^-$

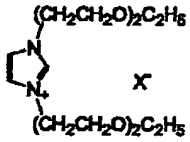
[0074]
[Formula 28]

(Y7) 

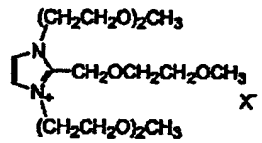
Y7-1 : X⁻=I^-
Y7-2 : X⁻=BF_4^-
Y7-3 : X⁻=$N^-(SO_2CF_3)_2$
Y7-4 : X⁻=CF_3COO^-
Y7-5 : X⁻=SCN^-

(Y8) 

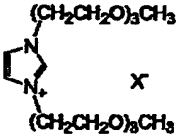
Y8-1 : X⁻=I^-
Y8-2 : X⁻=BF_4^-
Y8-3 : X⁻=$N^-(SO_2CF_3)_2$
Y8-4 : X⁻=PF_6^-
Y8-5 : X⁻=CF_3COO^-
Y8-6 : X⁻=SCN^-
Y8-7 : X⁻=$CF_3SO_3^-$

(Y9) 

Y9-1 : X⁻=I^-
Y9-2 : X⁻=BF_4^-
Y9-3 : X⁻=$N^-(SO_2CF_3)_2$
Y9-4 : X⁻=CF_3COO^-
Y9-5 : X⁻=SCN^-
Y9-6 : X⁻=$CF_3SO_3^-$

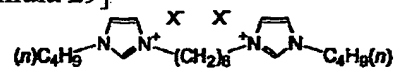
(Y10) 

Y10-1 : X⁻=I^-
Y10-2 : X⁻=BF_4^-
Y10-3 : X⁻=$N^-(SO_2CF_3)_2$

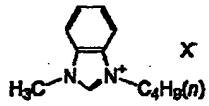
(Y11) 

Y11-1 : X⁻=I^-
Y11-2 : X⁻=BF_4^-
Y11-3 : X⁻=$N^-(SO_2CF_3)_2$

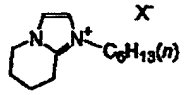
[0075]
[Formula 29]

(Y12) 

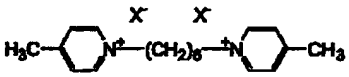
Y12-1 : X⁻=I⁻
Y12-2 : X⁻=BF_4^-
Y12-3 : X⁻=$N(SO_2CF_3)_2^-$

(Y13) 

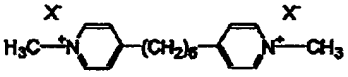
Y13-1 : X⁻=I⁻
Y13-2 : X⁻=BF_4^-
Y13-3 : X⁻=$N(SO_2CF_3)_2^-$

(Y14) 

Y14-1 : X⁻=I⁻
Y14-2 : X⁻=BF_4^-
Y14-3 : X⁻=$N(SO_2CF_3)_2^-$

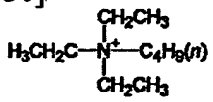
(Y15) 

Y15-1 : X⁻=I⁻
Y15-2 : X⁻=BF_4^-
Y15-3 : X⁻=$N(SO_2CF_3)_2^-$

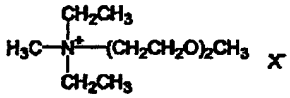
(Y16) 

Y16-1 : X⁻=I⁻
Y16-2 : X⁻=BF_4^-
Y16-3 : X⁻=$N(SO_2CF_3)_2^-$

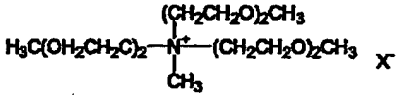
[0076]
[Formula 30]

(Y17) 

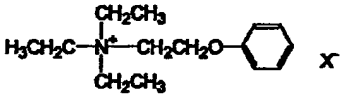
Y17-1 : X⁻=I⁻
Y17-2 : X⁻=BF_4^-
Y17-3 : X⁻=$N(SO_2CF_3)_2^-$
Y17-4 : X⁻=PF_6^-

(Y18) 

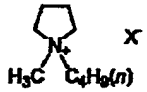
Y18-1 : X⁻=I⁻
Y18-2 : X⁻=BF_4^-
Y18-3 : X⁻=$N(SO_2CF_3)_2^-$

(Y19) 

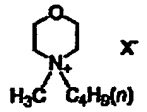
Y19-1 : X⁻=I⁻
Y19-2 : X⁻=BF_4^-
Y19-3 : X⁻=$N(SO_2CF_3)_2^-$
Y19-4 : X⁻=CF_3COO^-
Y19-5 : X⁻=SCN^-
Y19-6 : X⁻=$CF_3SO_3^-$

(Y20) 

Y20-1 : X⁻=I⁻
Y20-2 : X⁻=BF_4^-
Y20-3 : X⁻=$N(SO_2CF_3)_2^-$

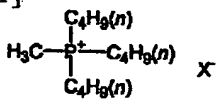
(Y21) 

Y21-1 : X⁻=I⁻
Y21-2 : X⁻=BF_4^-
Y21-3 : X⁻=$N(SO_2CF_3)_2^-$

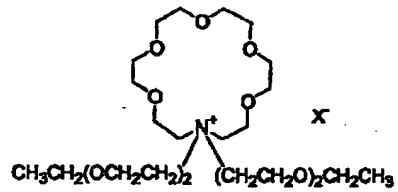
(Y22) 

Y22-1 : X⁻=I⁻
Y22-2 : X⁻=BF_4^-
Y22-3 : X⁻=$N(SO_2CF_3)_2^-$

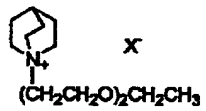
[0077]
[Formula 31]

(Y23) 

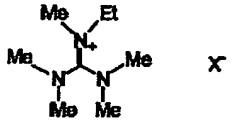
Y23-1 : X⁻=I⁻
Y23-2 : X⁻=BF_4^-
Y23-3 : X⁻=$N^-(SO_2CF_3)_2$

(Y24) 

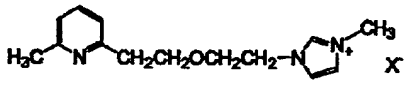
Y24-1 : X⁻=I⁻
Y24-2 : X⁻=BF_4^-
Y24-3 : X⁻=$N^-(SO_2CF_3)_2$

(Y25) 

Y25-1 : X⁻=I⁻
Y25-2 : X⁻=BF_4^-
Y25-3 : X⁻=$N^-(SO_2CF_3)_2$

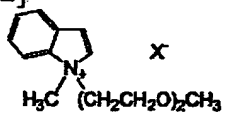
(Y25) 

Y26-1 : X⁻=I⁻
Y26-2 : X⁻=$N^-(SO_2CF_3)_2$
Y26-3 : X⁻=BF_4^-
Y26-4 : X⁻=PF_6^-

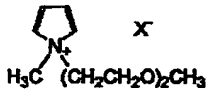
(Y27) 

Y27-1 : X⁻=I⁻
Y27-2 : X⁻=$N^-(SO_2CF_3)_2$
Y27-3 : X⁻=BF_4^-
Y27-4 : X⁻=CF_3COO^-
Y27-5 : X⁻=SCN^-
Y27-6 : X⁻=$CF_3SO_3^-$

[0078]
[Formula 32]

(Y28) 

Y28-1 : X⁻=I⁻
Y28-2 : X⁻=BF_4^-
Y28-3 : X⁻=$N^-(SO_2CF_3)_2$

(Y29) 

Y29-1 : X⁻=I⁻
Y29-2 : X⁻=BF_4^-
Y29-3 : X⁻=$N^-(SO_2CF_3)_2$

[0079] It is desirable not to use a solvent in this invention using what is in a melting state in ordinary temperature as an electrolyte salt. Although the solvent mentioned later may be added, as for the content of an electrolyte salt, it is desirable that it is more than 50 mass % to the whole electrolyte constituent, and it is desirable that it is especially more than 90 mass %. Moreover, as for the first of this invention, and second electrolyte constituents, it is desirable to contain the above-mentioned siloxane compound and iodine salts other than the above-mentioned polymer, and it is desirable that more than 50 mass % is an iodine salt among the salts to be used. Moreover, when using a solvent, it is desirable to make concentration of an electrolyte salt into 0.05 - 2 mol/l, and considering as 0.1 - 1.5 mol/l is more desirable.

[0080] (E) As for the first of an iodine this invention, and second electrolyte constituents, it is desirable to contain iodine. As for an iodine content, it is desirable that it is 0.1 to 20 mass % to the whole electrolyte constituent, and it is more desirable that it is 0.5 to 5 mass %. Moreover, iodine and a bromine can be added in the reaction solution containing the siloxane compound, electrophilic agent, and electrolyte salt which were mentioned above, and it can also be made to generate a redox couple beforehand. As for the concentration of the iodine in this reaction solution, or a bromine, considering as 0.01 - 0.3 mol/l is desirable.

[0081] (F) The first of a solvent this invention and second electrolyte constituents may contain the solvent. It is desirable that it is below the whole 50 mass %, as for the solvent content of an electrolyte constituent, it is more desirable that it is below 30 mass %, and it is desirable that it is especially below 10 mass %.
[0082] As a solvent, ionic mobility is high at hypoviscosity, or what can discover the ion conductivity which raised effective carrier concentration with the high dielectric constant, or was excellent since it was the both is desirable. as such a solvent -- a carbonate compound (ethylene carbonate --) Heterocyclic compounds, such as propylene carbonate (3-methyl-2-oxazolidinone etc.), ether compounds (a dioxane, diethylether, etc.) and chain-like ether (ethylene glycol dialkyl ether --) The propylene-glycol dialkyl ether, the polyethylene-glycol dialkyl ether, alcohols (a methanol --), such as the polypropylene-glycol dialkyl ether Ethanol, ethylene glycol monoalkyl ether, propylene-glycol monoalkyl ether, Polyethylene-glycol monoalkyl ether, polypropylene-glycol monoalkyl ether, etc., polyhydric alcohol (ethylene glycol, a propylene glycol, and a polyethylene glycol --) nitryl compounds (an acetonitrile --), such as a polypropylene glycol and a glycerol Guru taro dinitrile, a methoxy acetonitrile, a propionitrile, Ester (a carboxylate, phosphoric ester, phosphonate, etc.), such as a benzonitrile and screw cyano ethyl ether, non-proton nature polar solvents (dimethyl sulfoxide (DMSO), sulfolane, etc.), water, etc. are mentioned. Especially, a carbonate compound, a nitryl compound, and a heterocyclic compound are desirable. These solvents may mix and use two or more sorts if needed.
[0083] (G) In addition, to the first of this invention, and second electrolyte constituents, it is desirable to add basic compounds, such as t-butyl pyridine [of a publication (1997)], 2-picoline, 2, and 6-lutidine, to J.Am.Ceram.Soc., 80 (12), 3157-3171, etc. The desirable density ranges in the case of adding a basic compound are 0.05-2M.
[0084] In order to gel the first and second electrolyte constituents, technique, such as a polymerization of the monomers containing polymer addition, oil gelling agent addition, and polyfunctional monomer and crosslinking reaction of polymer, can be used together. When making it gel by polymer addition, the compound of a publication etc. is usable to "Polymer Electrolyte Reviews -1 and 2" (coeditorship of J.R.MacCallum and C.A.Vincent, ELSEVIER APPLIED SCIENCE), and it is desirable to use a polyacrylonitrile or a polyvinylidene fluoride. When making it gel by oil gelling agent addition, J.Chem.Soc.Japan, Ind.Chem.Sec., 46, and 779 (1943), J.Am.Chem.Soc., 111, and 5542 (1989), J.Chem.Soc., Chem.Commun., 1993, 390, Angew.Chem.Int.Ed.Engl., 35, and 1949 (1996), It is desirable to use the compound which can use the compound indicated by Chem.Lett., 1996, 885, J.Chem.Soc., Chem.Commun., 1997, and 545 grades, and has amide structure. Moreover, the method of gelling the electrolytic solution given in JP,11-185863,A and the method of gelling the quality of molten salt electrolysis given in JP,2000-58140,A are also applicable to this invention. moreover, the case where an electrolyte constituent is made to gel by the crosslinking reaction of polymer -- JP,2000-17076,A -- said -- the cross linking technique indicated by 2000-86724 is also applicable
[0085] [2] The optoelectric transducer of an optoelectric-transducer this invention has a conductive layer, a photosensitive layer, a charge transporting bed, and a counter electrode. As preferably shown in drawing 1 , a laminating is carried out to the order of a conductive layer 10, an under coat 60, a photosensitive layer 20, the charge transporting bed 30, and the counter electrode conductive layer 40, and a photosensitive layer 20 consists of charge transportation material 23 which permeated the opening between the semiconductor particle 21 by which sensitization was carried out with coloring matter 22, and the semiconductor particle 21 concerned. The charge transportation material 23 consists of the same component as the material used for the charge transporting bed 30. Moreover, in order to give intensity to an optoelectric transducer, you may form a substrate 50 as a ground of a conductive layer 10 and/or the counter electrode conductive layer 40. In this invention, it is arbitrary and the layer which consists the layer which consists of a conductive layer 10 and a substrate 50 to prepare of "a conductive base material", a counter electrode conductive layer 40, and a substrate 50 that it is arbitrary and is prepared is called "counter electrode." In addition, the conductive layer 10 in drawing 1 , the counter electrode conductive layer 40, and a substrate 50 may be transparent conductive-layer 10a, transparent counter electrode conductive-layer 40a, and transparent substrate 50a, respectively. That to which this optoelectric transducer is connected to an external load, and

electric work (power generation) is done is a photoelectric cell, and it is the photosensor which was made for the purpose of sensing of optical information.

[0086] In the optoelectric transducer of this invention shown in drawing 1 , when a semiconductor particle is n type, the light which carried out incidence to the photosensitive layer 20 containing the semiconductor particle 21 by which sensitization was carried out with coloring matter 22 excites coloring matter 22, and the electron of the high energy in the excited coloring matter 22 is passed to the conduction band of the semiconductor particle 21, and it reaches a conductive layer 10 by diffusion further. At this time, coloring matter 22 serves as an oxidant. In a photoelectric cell, while the electron in a conductive layer 10 works in an external circuit, it returns to the oxidant of coloring matter 22 through the counter electrode conductive layer 40 and the charge transporting bed 30, and coloring matter 22 is reproduced. A photosensitive layer 20 works as a negative electrode (optical anode), and a counter electrode 40 commits it as a positive electrode. On the boundaries (for example, the boundary of a conductive layer 10 and a photosensitive layer 20, the boundary of a photosensitive layer 20 and the charge transporting bed 30, the boundary of the charge transporting bed 30 and the counter electrode conductive layer 40, etc.) of each layer, the constituents of each class may be carrying out diffusive mixing mutually. Hereafter, each class is explained in detail.

[0087] (A) A conductive base material conductivity base material consists of the monolayer of (1) conductive layer or (2) conductive layers, and two-layer [of a substrate]. In the case of (1), that at which intensity and sealing performance are fully maintained as a material of a conductive layer can be used, for example, it can use metallic materials (platinum, gold, silver, copper, zinc, titanium, aluminum, these alloys, etc.). In the case of (2), the substrate which has a conductive layer containing an electric conduction agent can be used for a photosensitive-layer side. As a desirable electric conduction agent, metals (for example, platinum, gold, silver, copper, zinc, titanium, aluminum, an indium, the alloy containing these, etc.), carbon, and conductive metallic oxides (what doped a fluorine or antimony to an indium-tin multiple oxide and the tin oxide) are mentioned. The thickness of a conductive layer has desirable about 0.02-10 micrometers.

[0088] A conductive base material has surface electrical resistance as good as a low. Surface electrical resistance is below 50ohms / ** preferably, and is below 20ohms / ** more preferably.

[0089] When irradiating light from a conductive base material side, as for a conductive base material, it is desirable that it is substantially transparent. It means substantially that a light transmittance is it 10% or more that it is transparent in some or the whole region of a visible - near infrared region (400-1200nm). As for this light transmittance, it is desirable that it is 50% or more, and it is more desirable that it is 80% or more. It is desirable that the light transmittance of the wavelength region where a photosensitive layer has sensitivity especially is high.

[0090] What formed the transparent conductive layer which consists of a conductive metallic oxide in the front face of transparent substrates, such as glass and plastics, by an application or vacuum evaporationo as a transparent conductivity base material is desirable. As for a transparent conductive layer, it is desirable to consist of diacid-ized tin which doped a fluorine or antimony, or an indium-stannic-acid ghost (ITO). In addition to glass substrates, such as an advantageous soda glass and an alkali free glass without the influence of alkali elution, as a transparent substrate, a transparent polymer film is usable in respect of cost and intensity. As a material of a transparent polymer film, a triacetyl-cellulose (TAC), polyethylene-terephthalate (PET), polyethylenenaphthalate (PEN), syndiotactic polystyrene (SPS), polyphenylene-sulfide (PPS), polycarbonate (PC), polyarylate (PAr), polysulfone (PSF), polyester sulfone (PES), polyimide (PI), polyether imide (PEI), annular polyolefine, and bromine-ized phenoxy etc. is usable. In order to secure sufficient transparency, as for the coverage of a conductive metallic oxide, it is desirable to consider as per [0.01-100g] two 1m of base materials of glass or plastics.

[0091] It is desirable to use a metal lead in order to lower resistance of a transparent conductivity base material. The quality of the material of a metal lead has desirable metals, such as platinum, gold, nickel, titanium, aluminum, copper, and silver. As for a metal lead, it is desirable to install in a transparent substrate by vacuum evaporationo, sputtering, etc., and to prepare on it the transparent conductive layer which consists of conductive tin oxide or ITO. The fall of the amount of incident lights by metal lead installation is more preferably suppressed to 1 - 5% less than 10%.

[0092] (B) As for a photosensitive-layer (1) semiconductor photosensitive layer, it is desirable to contain the semiconductor particle by which sensitization was carried out with coloring matter. In a photosensitive layer, a semiconductor acts as a photo conductor, absorbs light, performs charge separation, and produces an electron and an electron hole. With the semiconductor by which coloring matter sensitization was carried out, generating of an optical absorption, the electron by this, and an electron hole takes place mainly in coloring matter, and a semiconductor bears the role which receives and transmits this electron (or electron hole). As for the semiconductor used by this invention, it is desirable that it is the n-type semiconductor which a conductor electron serves as a carrier under optical pumping, and gives an anode current.

[0093] The compounds (a strontium titanate, titanic-acid calcium, titanic-acid sodium, a barium titanate, niobic-acid potassium, etc.) which have an element semiconductor like silicon or germanium, a III-V system compound semiconductor, metaled chalcogenide (an oxide, a sulfide, selenides, those composites, etc.), and a perovskite structure as an example of the semiconductor used by this invention are mentioned. Metal chalcogenide is desirable especially.

[0094] As desirable metal chalcogenide, the oxide of titanium, tin, zinc, iron, a tungsten, a zirconium, a hafnium, strontium, an indium, a cerium, an yttrium, a lanthanum, vanadium, niobium, or a tantalum, cadmium, zinc, lead, silver, antimony or the sulfide of a bismuth, cadmium or a leaden selenide, the telluride of cadmium, etc. are mentioned. As other compound semiconductors, the selenide of phosphides, such as zinc, a gallium, an indium, and cadmium, a gallium arsenide, or a copper-indium, the sulfide of a copper-indium, etc. are mentioned. Furthermore, a composite like MxOySz or M1xM2yOz (an oxygen atom, x, and y and z express the number [atom / metal] with which M, M1, and M2 become, and, as for O, a valence becomes neutral, respectively) can also be used preferably.

[0095] Preferably the semiconductor used by this invention Si, TiO2, SnO2, Fe 2O3, WO3, ZnO, Nb 2O5, CdS, ZnS and PbS, Bi2S3, CdSe, CdTe, It is SrTiO3, GaP, InP, GaAs, CuInS2, or CuInSe2. More preferably TiO2, SnO2, Fe 2O3, WO3, ZnO, It is Nb 2O5, CdS and PbS, CdSe, SrTiO3 and InP, GaAs, CuInS2, or CuInSe2, is TiO2 or Nb 2O5 especially preferably, and is TiO2 most preferably. As for TiO2, it is desirable to include an anatase type crystal 70% or more, and it is more desirable that it is 100% anatase type crystal.

[0096] It is desirable to dope a metal in order to raise the electronic conductivity in a semiconductor. As a metal to dope, a divalent or trivalent metal is desirable. In order to prevent that a reverse current flows from a semiconductor to a charge transporting bed, it is also effective in a semiconductor to dope a univalent metal.

[0097] Although a single crystal or a polycrystal is sufficient as the semiconductor used for this invention, the polycrystal from a viewpoint of a manufacturing cost, raw-material reservation, and an energy pay back time is desirable. The amorphous portion may be included in part. As for a semiconductor, it is desirable to use as a porous membrane which consists of a semiconductor particle.

[0098] Generally the particle size of a semiconductor particle is the order of nm-mu m. As for the primary-particle mean particle diameter which asked for the projected area of a particle from the diameter when converting into a circle, it is desirable that it is 5-200nm, and it is more desirable that it is 8-100nm. Moreover, as for the mean particle diameter of the semiconductor particle in the dispersion liquid produced in order to apply on a conductive base material (aggregated particle), it is desirable that it is 0.01-30 micrometers. Two or more kinds of particles from which a particle size distribution differs may be mixed, it is desirable that the average size of a small particle is 25nm or less in this case, and it is more desirable that it is 10nm or less. Particle size is big, for example, it is also desirable to mix a semiconductor particle (100nm or more and about 300nm) in order to scatter an incident light and to raise the rate of optical capture.

[0099] You may mix and use two or more sorts of semiconductor particles from which a kind also differs. In such a case, as for one sort, it is desirable that they are TiO2, ZnO, Nb 2O5, or SrTiO3. As for another side, it is desirable that they are SnO2, Fe 2O3, or WO3. Especially, ZnO, SnO2, ZnO and WO3, ZnO, or the combination of SnO2 and WO3 is more desirable. When mixing and using two or more sorts of semiconductor particles, each particle size may differ. Especially the particle size of the

above Nb [TiO2, ZnO, and] 2O5 or SrTiO3 is large, and its small one is [the particle size of SnO2, Fe 2O3, or WO3] desirable. The large particle and large particle size of 100nm or more have [particle size] a desirable combination of a small particle 15nm or less.

[0100] a sol-gel method given [as a method of producing a semiconductor particle] in "the thin-layer-coating technology by the sol-gel method" (1995) etc. of the company (1998) of the "science of sol-gel method" AGUNE ** style of ********, and a technical-information association, and "composition of the monodisperse particle by the new synthesis method gel-sol method and size gestalt control" of Tadao Sugimoto -- wait -- the gel-sol method given in ****, the 35th volume, No. 9, 1012-1018 etc. pages (1996), Moreover, the method of producing an oxide for the chloride which Degussa developed by elevated-temperature hydrolysis in an acid hydrogen salt is also preferably applicable.

[0101] When a semiconductor particle is titanium oxide, each of above-mentioned sol-gel methods, gel-sol methods, and elevated-temperature adding-water part solution methods in the inside of the acid hydrogen salt of a chloride can be used preferably, and it is the Seino study further.

[Translation done.]

EXAMPLE

[Example] Hereafter, although an example explains this invention still in detail, this invention is not limited to them.

[0145] 1. The manufacture inside of titanium-dioxide dispersion liquid. With 15g [of titanium-dioxide particles] (product [made from Japanese Aerosil], Degussa P-25), 45g [of water], 1g [of dispersants] (Aldrich make, Triton X-100), and a diameter of 0.5mm zirconia-beads (Nikkato Corp. make) 30g was put into the container made from stainless steel of 200ml of content volume which carried out Teflon (registered trademark) coating, and distributed processing was carried out by 1500rpm for 2 hours using the Sand-grinder mill (product made from eye MEKKUSU). Filtration removed zirconia beads from the obtained dispersion liquid. The mean particle diameter of the titanium-dioxide particle in the obtained dispersion liquid was 2.5 micrometers. In addition, particle size was measured in the master sizer made from MALVERN.

[0146] 2. The glass rod was used and the above-mentioned dispersion liquid were applied to the electric conduction side side of the electrically conductive glass (thing and surface-electrical-resistance about 30ohm/** which carried out cutting processing of the TCO glass [by Asahi Glass Co., Ltd.]-U at the 20mmx20mm size) which has the tin-oxide layer which doped the creation fluorine of TiO2 electrode which adsorbed coloring matter. The coverage of a semiconductor particle was taken as 20 g/m2. At that time, the adhesive tape was stretched to the part by the side of an electric conduction side (from an edge to 3mm), and it considered as the spacer, and glass was put in order and it applied eight sheets at a time at once so that an adhesive tape might come to ends. After the application, it exfoliated and the adhesive tape was air-dried for one day at the room temperature. Next, this glass was put into the electric furnace (muffle furnace FP-32 type made from Yamato Science), it calcinated for 30 minutes at 450 degrees C, and TiO2 electrode was obtained. It flooded with the ethanol solution (3x10-4 mol/l) of coloring matter R-1 for 3 hours, after taking out this electrode and cooling. TiO2 electrode which coloring matter dyed was washed and air-dried by ethanol, after being immersed in the 4-t-butyl pyridine for 15 minutes. The thickness of the obtained photosensitive layer was 6.5 micrometers.

[0147] 3. The acetonitrile solution containing the electrolyte salt MHIm of the photoelectrochemical-cell examples 1-7, the example 1 of comparison, and 20.5 mol/l using the electrolyte constituent containing the production 3-1. solvent of a photoelectrochemical cell (iodine salt of 1-methyl-3-hexyl imidazolium) and 0.05 mol [/l.] iodine was prepared, and the siloxane compound 1-4 was added to this. 10 mass % The siloxane compound made the [solvent + electrolyte salt + siloxane compound] 100 mass %, and used it here. It was made to sink into the crevice which piled up the platinum vacuum evaporationo glass of the coloring matter sensitization TiO2 electrode substrate (20mmx20mm) which produced the obtained solution as mentioned above, and the same size as this using capillarity, introduced into the TiO2 electrode, it closed by the epoxy system encapsulant, and the photoelectrochemical cell of an example 1 using the first electrolyte constituent of this invention was obtained. The photoelectrochemical cell of examples 2-7 using the first electrolyte constituent of this invention was obtained like the above-mentioned example 1 except having changed the solvent and the siloxane compound, as shown in the following table 1. Moreover, except not adding a siloxane compound, the photoelectrochemical cell of the example 1 of comparison was produced like the above-mentioned example 1, and the photoelectrochemical cell of the example 2 of comparison was produced like the above-mentioned example 1 except having changed to the siloxane compound

further and having added t-butyl pyridine. The coloring matter used for the photoelectrochemical cell of the above-mentioned examples 1-7 and the examples 1 and 2 of comparison, a siloxane compound and its mass ratio, an electrolyte salt and its concentration, the concentration of iodine, and a solvent are collectively shown in Table 1. In addition, AN in Table 1 expresses an acetonitrile, NMO expresses 3-methyl-2-oxazolidinone, PC expresses propylene carbonate, and MHIm expresses the iodine salt of 1-methyl-3-hexyl imidazolium. Moreover, the mass ratio of a siloxane compound is a mass ratio at the time of making a [solvent + electrolyte salt + siloxane compound] into 100 mass % among Table 1.

[0148]

[Table 1]

光電気化学電池	色素	シロキサン化合物 (質量%)	電解質塩 (mol/l)	ヨウ素 (mol/l)	溶媒
実施例1	R-1	1-4 (10)	MHIm (0.5)	0.05	AN
実施例2	R-1	1-4 (10)	MHIm (0.5)	0.05	NMO
実施例3	R-1	1-4 (10)	MHIm (0.5)	0.05	PC
実施例4	R-1	1-6 (10)	MHIm (0.5)	0.05	AN
実施例5	R-1	1-11 (10)	MHIm (0.5)	0.05	AN
実施例6	R-1	1-13 (10)	MHIm (0.5)	0.05	AN
実施例7	R-1	1-17 (10)	MHIm (0.5)	0.05	AN
比較例1	R-1	なし	MHIm (0.5)	0.05	AN
比較例2	R-1	t-ブチルピリジン (10)	MHIm (0.5)	0.05	AN

[0149] The acetonitrile solution containing the electrolyte salt MHIm of an example 8 - 170.5 mol/l (iodine salt of 1-methyl-3-hexyl imidazolium) and the iodine of 0.05 mol/l was prepared. The siloxane compound 1-4 was added to this solution, the electrophilic agent E-3 was mixed further, and the uniform solution was adjusted. Here, the siloxane compound made the [solvent + electrolyte salt + siloxane compound] 100 mass %, 10 mass % Used it, and it added the electrophilic agent so that the mole ratio of the electrophilic part of the electrophilic agent to the reactive site of a siloxane compound might be set to 1. It was made to sink into the crevice which piled up the platinum vacuum evaporationo glass of the coloring matter sensitization TiO2 electrode substrate (20mmx20mm) which produced the obtained solution as mentioned above, and the same size as this using capillarity, and introduced into the TiO2 electrode. This was left at 50 degrees C for 12 hours, polymerization reaction was performed, it closed by the epoxy system encapsulant, and the photoelectrochemical cell of an example 8 using the second electrolyte constituent of this invention was obtained. The photoelectrochemical cell of examples 9-14 using the second electrolyte constituent of this invention was obtained like the above-mentioned example 8 except having changed a solvent, a siloxane compound, and an electrophilic agent and its mole ratio, as shown in the following table 2. Moreover, it changed to what shows a siloxane compound in Table 2, and the photoelectrochemical cell of examples 15-17 using the second electrolyte constituent of this invention was obtained like the above-mentioned example 8 except having made the amount of the electrophilic agent used into 5 mass % to the siloxane compound. The coloring matter used for the photoelectrochemical cell of the above-mentioned examples 8-17, an electrophilic agent and its mole ratio, a siloxane compound and its mass ratio, an electrolyte salt and its concentration, the concentration of iodine, and a solvent are collectively shown in Table 2. In addition, AN in Table 2 expresses an acetonitrile, NMO expresses 3-methyl-2-oxazolidinone, PC expresses propylene carbonate, and MHIm expresses the iodine salt of 1-methyl-3-hexyl imidazolium. Moreover, among Table 2, the mass ratio of a siloxane compound is a mass ratio at the time of making a [solvent + electrolyte salt + siloxane compound] into 100 mass %, and the mole ratio of an electrophilic agent is a mole ratio of the electrophilic part of the electrophilic agent to the reactive site of a siloxane compound. However, not a mole ratio but the mass ratio (wt%) to a siloxane compound shows the amount of the electrophilic agent used used for the photoelectrochemical cell of examples 15-17.

[0150]

[Table 2]

光電気化学電池	色素	求電子剤 (モル比又は質量比)	シロキサン化合物 (質量%)	電解質塩 (mol/l)	ヨウ素 (mol/l)	溶媒
実施例8	R-1	E-3 (1)	1-4 (10)	MHIm (0.5)	0.05	AN
実施例9	R-1	E-3 (1)	1-4 (10)	MHIm (0.5)	0.05	NMO
実施例10	R-1	E-3 (1)	1-4 (10)	MHIm (0.5)	0.05	PC
実施例11	R-1	E-3 (1)	1-6 (10)	MHIm (0.5)	0.05	AN
実施例12	R-1	E-12 (1)	1-4 (10)	MHIm (0.5)	0.05	AN
実施例13	R-1	E-12 (1)	1-6 (10)	MHIm (0.5)	0.05	AN
実施例14	R-1	E-3 (0.9), E-5 (0.1)	1-4 (10)	MHIm (0.5)	0.05	AN
実施例15	R-1	E-3 (5 wt%)	1-11 (10)	MHIm (0.5)	0.05	AN
実施例16	R-1	E-3 (5 wt%)	1-13 (10)	MHIm (0.5)	0.05	AN
実施例17	R-1	E-3 (5 wt%)	1-17 (10)	MHIm (0.5)	0.05	AN

[0151] The hexa ethylene glycol methacrylic ester ("BUREMMA PE-350" by the Nippon Oil & Fats chemistry company) of 3500mg of examples of comparison, 1g propylene carbonate, and the mixed liquor containing the 2mg polymerization initiator azobisuisobutironitoriru were prepared, and the 500mg iodation lithium was dissolved in this. Next, the vacuum deairing of this mixed liquor was carried out for 10 minutes, and it applied to the coloring matter sensitization TiO2 electrode substrate (20mmx20mm) produced as mentioned above. Then, after putting under reduced pressure of TiO2 electrode which applied mixed liquor and urging osmosis of a monomer except for the air bubbles in TiO2 electrode, at 60 degrees C, it heated for 1 hour and the polymerization was carried out. It **(ed) for 30 minutes under iodine atmosphere at the room temperature after the polymerization, and iodine was diffused in the obtained polymer. This was piled up with the counter electrode which deposited platinum, and the photoelectrochemical cell (photoelectrochemical cell using the electrolyte the Chemical Society of Japan, 7, and given in 484 page (1997)) of the example 3 of comparison was obtained.

[0152] 3-2. The fused salt A of the photoelectrochemical-cell examples 18-28 and the example 4 of comparison - 660 mass % using the electrolyte constituent containing room temperature fused salt, the fused salt B of 28 mass %, the iodine of 2 mass %, and the siloxane compound 1-4 of 10 mass % were mixed, and the uniform electrolyte constituent was prepared. After applying 5micro of obtained electrolyte constituents 1 to the coloring matter sensitization TiO2 electrode substrate produced as mentioned above, it put under reduced pressure of this electrode, and the electrolyte constituent was made to permeate. After the electrolyte constituent fully permeated and the air in an electrode fell out, platinum vacuum evaporationo glass was laid on top of this, and the photoelectrochemical cell of an example 18 using the first electrolyte constituent of this invention was obtained. The photoelectrochemical cell of examples 19-28 using the first electrolyte constituent of this invention was obtained like the above-mentioned example 18 except having changed fused salt, its mass ratio, and the siloxane compound, as shown in the following table 3. Moreover, don't add a siloxane compound but fused salt and its mass ratio should be shown in Table 3. Except having changed, the photoelectrochemical cell of the examples 4 and 5 of comparison was produced like the above-mentioned example 18, it changed to the siloxane compound further, t-butyl pyridine was added, and the photoelectrochemical cell of the example 6 of comparison was produced like the above-mentioned example 18 except having changed fused salt and its mass ratio, as shown in Table 3. However, the amount of t-butyl pyridine was made into 10 mass %. The coloring matter used for the photoelectrochemical cell of the above-mentioned examples 18-28 and the examples 4-6 of comparison, fused salt and its mass ratio, the mass ratio of iodine, a siloxane compound, and its mass ratio are collectively shown in Table 3. Moreover, the structure of fused salt A-D is shown below.

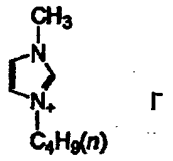
[0153]

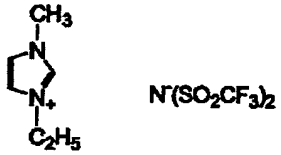
[Table 3]

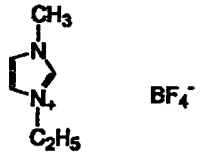
光電気化学電池	色素	溶融塩 (質量%)	ヨウ素 (質量%)	シロキサン化合物 (質量%)
実施例18	R-1	A (60) / B (28)	2	1-4 (10)
実施例19	R-1	A (60) / C (28)	2	1-4 (10)
実施例20	R-1	A (60) / C (28)	2	1-4 (10)
実施例21	R-1	A (60) / B (28)	2	1-6 (10)
実施例22	R-1	D (60) / C (28)	2	1-4 (10)
実施例23	R-1	D (60) / C (28)	2	1-4 (10)
実施例24	R-1	D (60) / C (28)	2	1-6 (10)
実施例25	R-1	D (60) / C (28)	2	1-4 (10)
実施例26	R-1	A (60) / C (28)	2	1-11 (10)

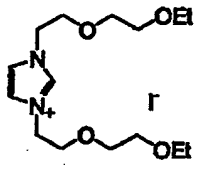
実施例27	R-1	A (60) / C (28)	2	1-13 (10)
実施例28	R-1	A (60) / C (28)	2	1-17 (10)
比較例4	R-1	A (70) / C (28)	2	なし
比較例5	R-1	D (70) / C (28)	2	なし
比較例6	R-1	A (60) / C (28)	2	t-ブチルピリジン

[0154]
[Formula 39]

A 

B 

C 

D 

[0155] The fused salt A of an example 29 - 3960 mass %, the fused salt B of 28 mass %, the iodine of 2 mass %, and the siloxane compound 1-4 of 10 mass % were mixed, the electrophilic agent E-3 was added further, and the uniform electrolyte constituent was prepared. Here, the electrophilic agent was added so that the mole ratio of the electrophilic part of the electrophilic agent to the reactive site of a siloxane compound might be set to 1. After applying 5micro of obtained electrolyte constituents l to the coloring matter sensitization TiO2 electrode substrate produced as mentioned above, it put under reduced pressure of this electrode, and the electrolyte constituent was made to permeate. After the electrolyte constituent fully permeated and the air in an electrode fell out, platinum vacuum evaporationo glass was laid on top of this, it was left at 50 degrees C for 10 hours, polymerization reaction was performed, and the photoelectrochemical cell of an example 29 using the second electrolyte constituent of this invention was obtained. The photoelectrochemical cell of examples 30-39 using the second electrolyte constituent of this invention was obtained like the above-mentioned example 29 except having changed fused salt, siloxane compounds and those mass ratios, and an electrophilic agent and its mole ratio, as shown in the following table 4. The coloring matter used for the photoelectrochemical cell of the above-mentioned examples 29-39, fused salt and its mass ratio, the mass ratio of iodine, an electrophilic agent, its mole ratio, a siloxane compound, and its mass ratio are collectively shown in Table 4. In addition, the mole ratio of an electrophile agent is a mole ratio of the electrophilic part of the electrophile agent to the reactive site of a siloxane compound among Table 4.
[0156]
[Table 4]

光電気化学電池	色素	溶融塩 (質量%)	ヨウ素 (質量%)	求電子剤 (モル比)	シロキサン化合物 (質量%)
実施例29	R-1	A (60) / B (28)	2	E-3 (1)	1-4 (10)
実施例30	R-1	A (60) / C (28)	2	E-3 (1)	1-4 (10)
実施例31	R-1	A (60) / C (28)	2	E-12 (1)	1-4 (10)
実施例32	R-1	A (60) / B (28)	2	E-3 (1)	1-6 (10)
実施例33	R-1	D (60) / C (28)	2	E-3 (1)	1-4 (10)
実施例34	R-1	D (60) / C (28)	2	E-12 (1)	1-4 (10)
実施例35	R-1	D (60) / C (28)	2	E-3 (1)	1-6 (10)
実施例36	R-1	D (60) / C (28)	2	E-3 (0.9), E-5 (0.1)	1-4 (10)
実施例37	R-1	A (60) / C (28)	2	E-3 (1)	1-11 (10)
実施例38	R-1	A (60) / C (28)	2	E-3 (1)	1-13 (10)
実施例39	R-1	A (60) / C (28)	2	E-3 (1)	1-17 (10)

[0157] The photoelectrochemical cell of the example 7 of comparison was produced like the above-mentioned example 3 of comparison except having changed to example of comparison 7 propylene carbonate, and having used the above-mentioned compound C.

[0158] 4. The simulation sunlight which does not include ultraviolet rays was generated by letting AM1.5 filter (product made from Oriel), and a sharp cut filter (Kenko L-42) pass for the light of the xenon lamp of measurement 500W of a photoelectric conversion efficiency (product made from USHIO Electrical and electric equipment). This luminous intensity was 86 mW/cm2. The electrical and electric equipment which irradiated the photoelectrochemical cell of the examples 1-39 produced at 50 degrees C and the examples 1-7 of comparison, and generated this simulation sunlight was measured in the current-potential measuring device (case rhe SMU238 type). The decreasing rate of the short-circuit current density (Jsc) of each photoelectrochemical cell called for by this, an open circuit voltage (Voc), a form factor (FF), a conversion efficiency (eta), and the conversion efficiency after 360-hour continuous irradiation is shown in Tables 5-8.

[0159]

[Table 5]

光電気化学電池	短絡電流密度 (Jsc) mA/cm^2	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (360時間後) %
実施例1	10.1	0.72	0.62	5.24	78
実施例2	9.75	0.72	0.61	4.98	76
実施例3	9.89	0.73	0.62	5.20	77
実施例4	10.2	0.72	0.61	5.21	76
実施例5	9.62	0.73	0.60	4.90	78
実施例6	9.43	0.74	0.61	4.95	78
実施例7	9.67	0.73	0.60	4.92	77
比較例1	9.92	0.65	0.65	4.87	99
比較例2	9.42	0.72	0.61	4.81	99

[0160]

[Table 6]

光電気化学電池	短絡電流密度 (Jsc) mA/cm^2	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (360時間後) %
実施例8	9.12	0.68	0.57	4.11	42
実施例9	8.97	0.67	0.58	3.86	38
実施例10	8.89	0.67	0.56	3.82	35
実施例11	9.10	0.66	0.57	3.98	41
実施例12	9.12	0.68	0.58	4.04	37
実施例13	9.10	0.66	0.56	3.91	33
実施例14	9.11	0.67	0.58	3.97	29
実施例15	7.67	0.68	0.56	3.40	33
実施例16	7.58	0.69	0.57	3.47	35
実施例17	7.90	0.68	0.57	3.58	37
比較例3	2.22	0.64	0.65	1.07	82

[0161]

[Table 7]

光電気化学電池	短絡電流密度 (Jsc) mA/cm^2	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (380時間後) %
実施例18	9.11	0.61	0.57	3.68	18
実施例19	9.08	0.62	0.58	3.80	18
実施例20	9.20	0.62	0.58	3.85	16
実施例21	9.11	0.60	0.58	3.69	17
実施例22	9.28	0.60	0.57	3.69	17
実施例23	9.14	0.60	0.58	3.70	16
実施例24	9.13	0.61	0.57	3.69	16
実施例25	9.09	0.61	0.58	3.74	14
実施例26	8.10	0.62	0.58	3.39	15
実施例27	8.99	0.60	0.57	3.58	16
実施例28	8.98	0.61	0.57	3.63	15
比較例4	7.85	0.52	0.58	2.75	35
比較例5	7.90	0.55	0.59	2.98	30
比較例6	7.20	0.62	0.58	2.91	45

[0162]
[Table 8]

光電気化学電池	短絡電流密度 (Jsc) mA/cm^2	開放電圧 (Voc) V	形状因子 (FF)	変換効率 (η) %	η低下率 (380時間後) %
実施例29	8.11	0.57	0.55	2.96	18
実施例30	8.20	0.59	0.55	3.09	18
実施例31	8.20	0.59	0.54	3.03	16
実施例32	8.09	0.55	0.55	2.85	17
実施例33	8.28	0.60	0.55	3.18	17
実施例34	8.28	0.61	0.54	3.17	16
実施例35	8.25	0.58	0.55	3.08	16
実施例36	8.27	0.58	0.54	3.01	14
実施例37	8.01	0.60	0.55	2.64	15
実施例38	7.11	0.61	0.54	2.72	14
実施例39	7.05	0.60	0.54	2.66	15
比較例7	1.40	0.52	0.50	0.42	14

[0163] To this causing [the open circuit voltage] a low photoelectric conversion efficiency low, as for the photoelectrochemical cell of the examples 1, 4, and 5 of comparison, an open circuit voltage is high and the conversion efficiency of the photoelectrochemical cell [the examples 1-7 and the photoelectrochemical cell of 18-28] using the first electrolyte constituent of this invention is improving in connection with it so that more clearly than Table 5 and 7. Moreover, although degradation after dark place preservation is remarkable in the photoelectrochemical cell of the examples 1 and 2 of comparison which contain many organic solvents in an electrolyte constituent, and examples 1-7, by using the first electrolyte constituent of this invention shows that endurance is improved. Moreover, Table 6 and 8 shows that the examples 8-17 and the photoelectrochemical cell of 29-39 using the second electrolyte constituent of this invention show the outstanding conversion efficiency and outstanding endurance as compared with the photoelectrochemical cell of the examples 3 and 7 of comparison using the conventional solid electrolyte.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.
[Drawing 2] It is the fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.
[Drawing 3] It is the fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.
[Drawing 4] It is the fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.
[Drawing 5] It is the fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.
[Drawing 6] It is the fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.
[Drawing 7] It is the fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.
[Drawing 8] It is the fragmentary sectional view showing the structure of the desirable optoelectric transducer of this invention.
[Description of Notations]
10 ... Conductive layer
10a ... Transparent conductive layer
11 ... Metal lead
20 ... Photosensitive layer
21 ... Semiconductor particle
22 ... Coloring matter
23 ... Charge transportation material
30 ... Charge transporting bed
40 ... Counter electrode conductive layer
40a ... Transparent counter electrode conductive layer
50 ... Substrate
50a ... Transparent substrate
60 ... Under coat

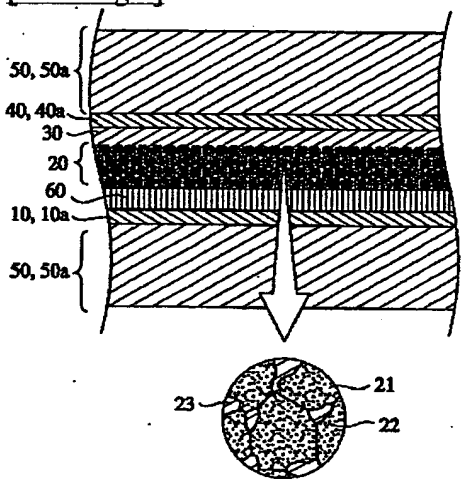
[Translation done.]

* NOTICES *

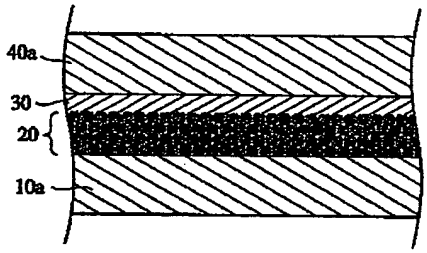
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



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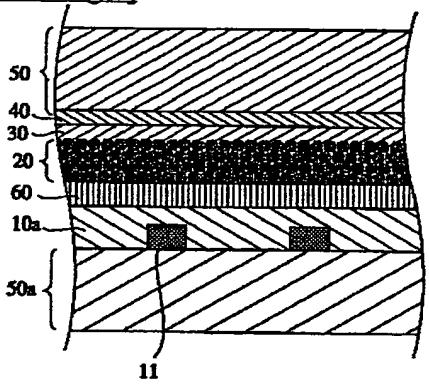

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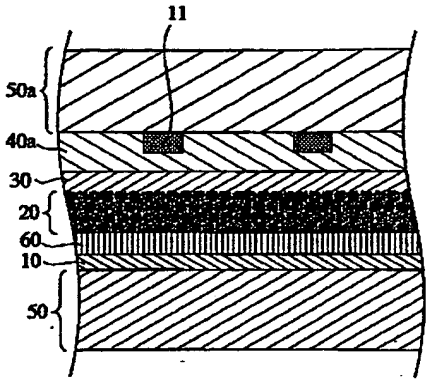
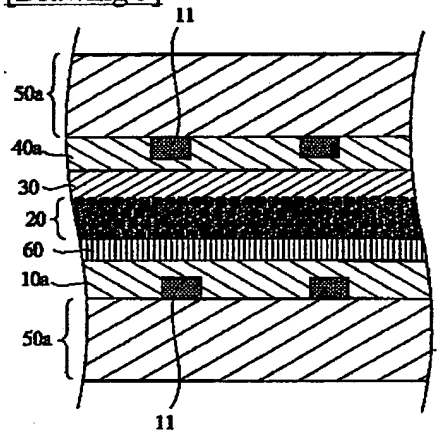


[Drawing 5]



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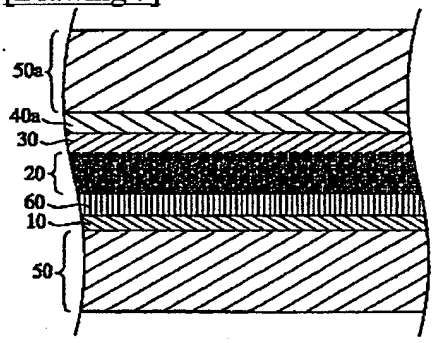

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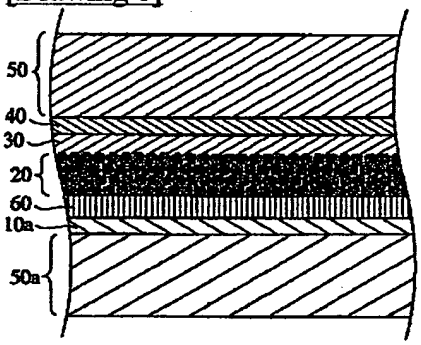
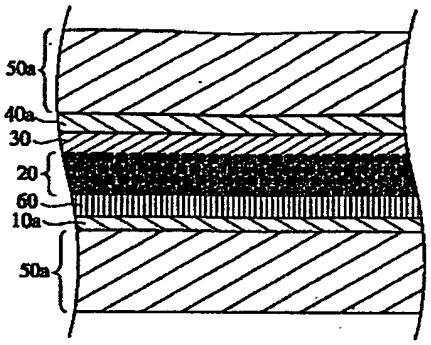


[Drawing 8]



[Translation done.]